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Tailored Production of Sustainable Low-Cost Lignocellulosic Advanced Biofuel Blends as Diesel and Petrol Substitutes

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Declaration

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Summary

This thesis advances the production and understanding of alkyl levulinates from lignocellulosic biomass via ethanolysis and butanolysis, delivering four key contributions.

It established steady-state operation for alcoholysis reactions, providing the first systematic demonstration of steady-state conditions for alcoholysis reactions under defined conditions. Earlier studies typically reported values at arbitrary time points without distinguishing between kinetic and steady-state phases. By defining conditions under which steady-state is achieved, this work created a rigorous benchmark for yield determination and enabled robust comparison across conditions and substrates, including the model carbohydrates and the lignocellulosic feedstock investigated here, corn cob.

Building on this, the second contribution introduced a new framework for yield representation. The alcoholysis studies revealed for the first time that alkyl levulinates originate from both cellulose and hemicellulose, requiring a redefinition of molar yield normalisation to reflect both contributors accurately. Alongside this, the work quantified previously neglected co-products, most notably dialkyl ethers, which, together with levulinates and residual alcohols, form the three-component blends that can be used as blending components (demonstrated stable up to ~25 vol% in diesel). Additional co-products such as n-butyl acetate and n-butyl formate were also identified, expanding the known product spectrum and strengthening the basis for techno-economic evaluation.

The third contribution is the determination, under clearly defined one-pot conditions, of the minimum acid charge required to catalyse the alcoholysis of a real lignocellulosic feedstock (corn cob). Because one-pot alcoholysis of whole biomass remains comparatively understudied, this threshold had not been established. Our results show that a non-trivial fraction of the acid is irreversibly consumed by interactions with the biomass matrix, so a baseline acidity must be supplied before productive conversion can proceed. Quantifying this requirement provides actionable guidance for catalyst utilisation and delivers data directly relevant to process design, technoeconomic modelling, and sustainability assessment.

Finally, the thesis developed and validated a surrogate kinetic modelling approach based on molecular group additivity and hierarchical representation. Calibrated to glucose, cellulose, xylan, and corn cob, the model reproduced yields and product distributions for both ethanolysis and butanolysis processes and linked biochemical composition to predicted outcomes. While Chapter 4 characterised a broader set of Annex IX feedstocks, these remain to be tested experimentally, providing a basis for future validation and extension of the modelling framework.

Together, these advances move alcoholysis from laboratory feasibility towards industrial relevance. They clarify what can be achieved under steady-state operation, establish a comprehensive and accurate yield framework, quantify neglected co-products of practical importance, and introduce predictive modelling tools that bridge laboratory data with process optimisation. More broadly, this thesis demonstrates how rigorous experimentation and modelling can transform alcoholysis from an empirical observation into a predictable, scalable, and strategically relevant pathway for advanced biofuel production.

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Chapter 1

Introduction

1.1 Global Energy Outlook

The global energy system is at the centre of the climate crisis, with fossil fuel combustion driving greenhouse gas emissions and intensifying the need for urgent decarbonisation. To address this escalating crisis, the Paris Agreement was adopted in December 2015 and entered into force in November 2016. It aims to limit global temperature rise to well below 2°C above pre-industrial levels, with efforts to stay below 1.5°C [1]. The agreement represents a near-universal commitment to climate action, requiring countries to submit nationally determined contributions (NDCs), which are reviewed and strengthened every five years. Developed nations are obligated to provide financial and technical support to developing countries, including a target of mobilising \$100 billion annually. The agreement also facilitates voluntary carbon markets, encourages the conservation of carbon sinks, and recognises the importance of loss and damage from climate impacts. It actively involves non-state actors, such as businesses and cities, through platforms like the Non-State Actor Zone for Climate Action (NAZCA).

Despite progress in decarbonising electricity via renewables, other sectors remain hard to abate. Transport is challenging to electrify beyond light vehicles, particularly in aviation, shipping, and freight. Manufacturing and construction rely heavily on fossil fuels for heat and materials processing. Agriculture presents inherent emissions from livestock and land use change. Addressing these complex sectors requires scalable, low-carbon solutions. Advanced biofuels offer a promising pathway, particularly where electrification and direct decarbonisation are not viable.

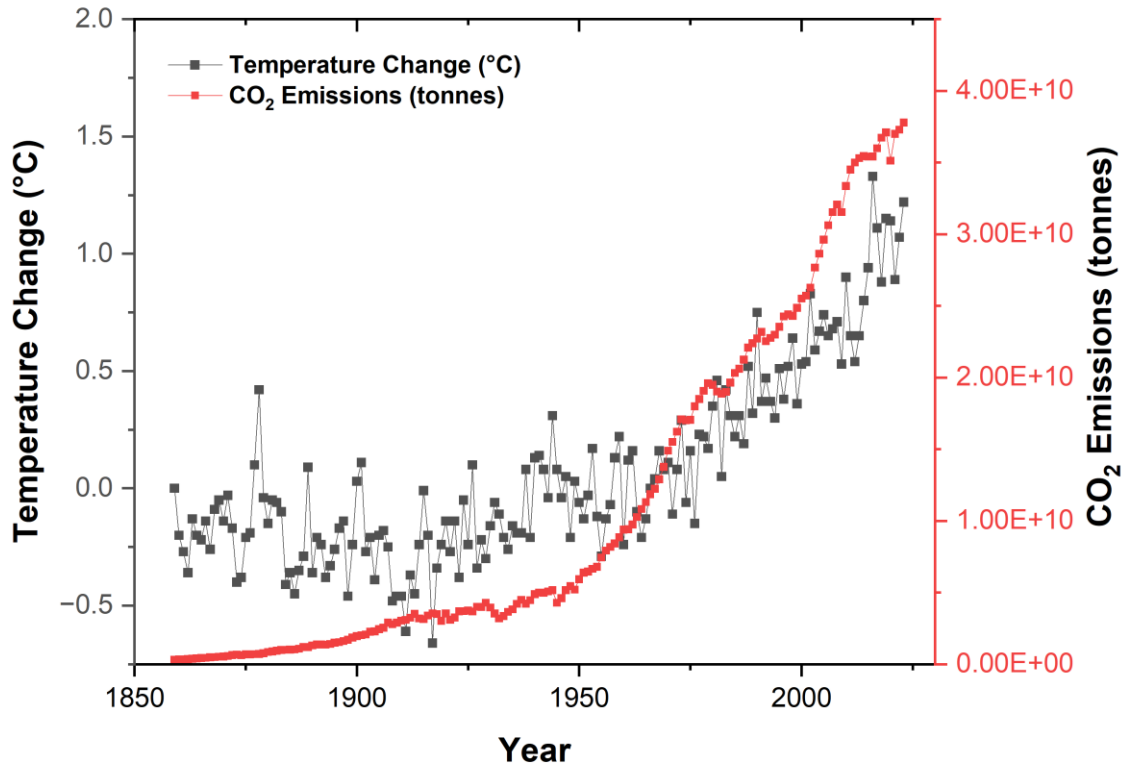


Figure 1. Temperature change (°C) since pre-industrial levels and anthropogenic carbon dioxide emissions as a function of time [2].

1.2 Challenges in Decarbonising the Transport Sector

Decarbonising the transport sector presents a multifaceted challenge shaped by technological, infrastructural, economic, and behavioural barriers. Unlike the electricity sector, which has successfully integrated renewable energy sources, transport remains heavily reliant on fossil fuels. According to *Our World in Data*, transport accounted for approximately 15.5% of global greenhouse gas emissions in 2021 [2]. This reliance stems largely from the unique energy demands of long-haul transport, such as aviation, maritime shipping, and heavy freight, which currently lack scalable, low-carbon alternatives. The high energy density of liquid fossil fuels makes them difficult to replace in these contexts. Battery technologies, while improving, are insufficient for the long distances and payloads involved, and though biofuels and synthetic e-fuels hold promise, they are not yet economically viable or available at the necessary scale [3, 4].

World Greenhouse Gas Emissions by Sector (2021)

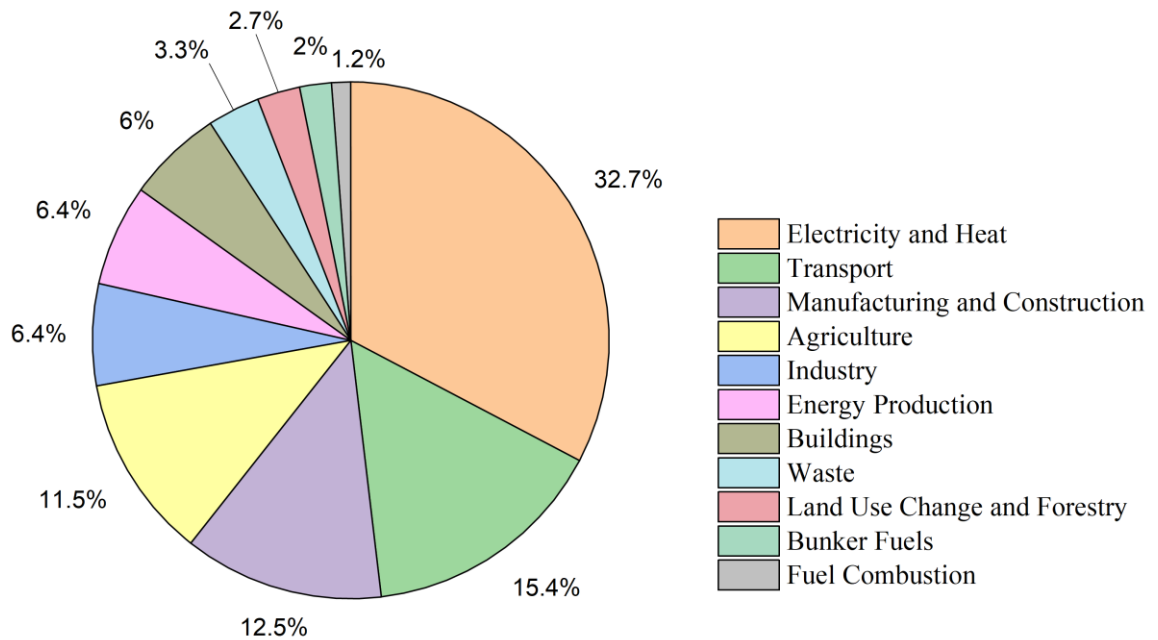


Figure 2. Global greenhouse gas emissions by sector in CO₂-equivalent, based on 2021 data from Our World in Data [2].

A major structural challenge is the longevity of transport assets, and the infrastructure designed to support them. Commercial aircraft have operational lifespans exceeding 25 years, while conventional internal combustion engine (ICE) vehicles typically remain in use for over a decade [5]. This asset lock-in means that even with an immediate pivot to zero-emission vehicles (ZEVs), the existing fleet will continue emitting CO₂ well into the future. Moreover, the physical infrastructure underpinning the transport system, such as roads, fuelling stations, maintenance networks, and logistics chains, has been optimised for fossil fuel use. Transitioning to alternatives like electric or hydrogen-powered vehicles necessitates large-scale investments in new infrastructure, including charging networks and hydrogen refuelling stations, all of which require long-term planning, regulatory support, and significant public and private capital [5].

Economic and supply chain constraints further complicate the transition. Upfront costs for electric and hydrogen-powered vehicles remain high relative to traditional internal combustion engine models, posing affordability challenges for consumers and businesses alike, especially in emerging economies [5, 6]. These vehicles also depend on critical raw materials such as lithium, cobalt, and rare earth elements, the supply of which is geographically concentrated and subject to geopolitical and environmental risks. At the same

time, increased electrification of transport places additional demand on electricity grids, requiring concurrent expansion in low-carbon energy generation and grid resilience. Without proactive investment in energy infrastructure and raw material supply chains, the deployment of clean transport technologies may stall [7, 8].

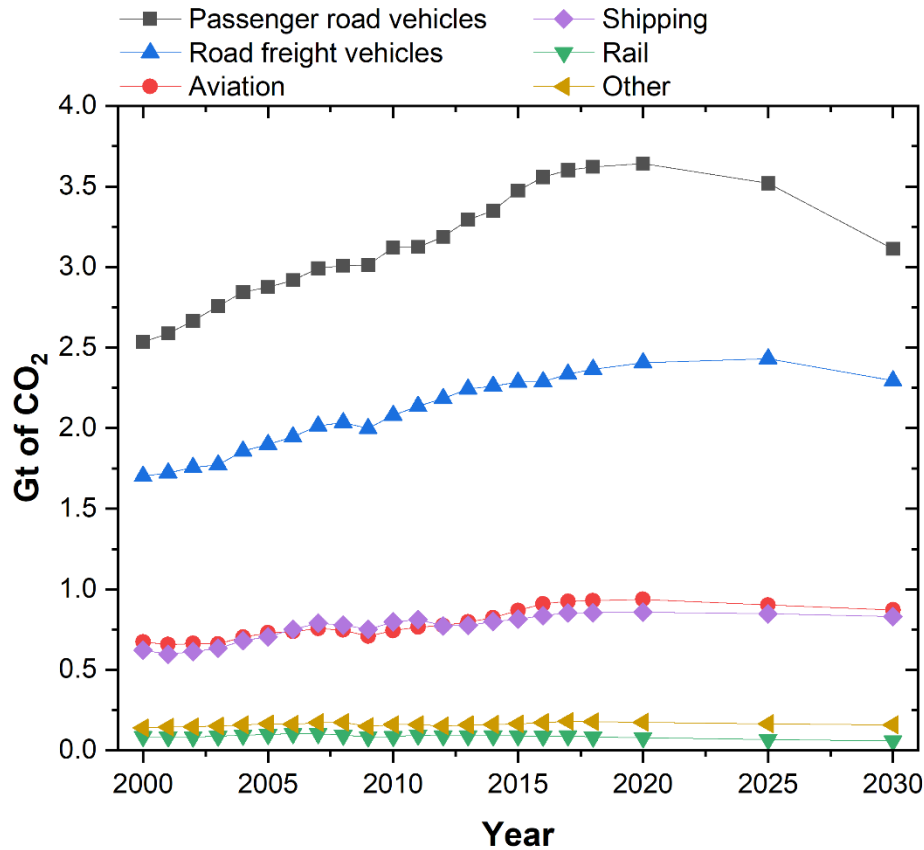


Figure 3. Global greenhouse gas observed and predicted emissions by sector in 2021 according to Our World in Data [2].

Finally, behavioural and policy-related factors play a critical role in shaping the pace of decarbonisation. Consumer hesitancy surrounding range anxiety, charging times, and the total cost of ownership of electric vehicles persists, particularly in areas where charging infrastructure is underdeveloped [6, 9]. Inconsistent or short-term policy signals from governments can undermine investor confidence and slow the deployment of alternative technologies. Additionally, entrenched interests in the fossil fuel and automotive sectors can resist regulatory changes that disrupt existing business models [5]. Addressing these challenges will require robust, long-term policy frameworks that support innovation, incentivise adoption, and manage the socioeconomic impacts of the transition. The following

section explores the suite of technological, infrastructural, and policy options available to decarbonise the transport sector and overcome these interlinked obstacles.

1.3 Solutions for Decarbonising Transport

1.3.1 Electric Vehicles

Electric vehicles (EVs) are a key technology in the transition to low-emission transport, offering no tailpipe emissions and much higher energy efficiency than internal combustion engine vehicles. With electric drivetrains achieving around 60–70% efficiency, electric vehicles contribute significantly to reducing urban air pollution and lifecycle greenhouse gas (GHG) emissions, particularly when powered by renewable electricity [10]. They also offer reduced running and maintenance costs due to fewer moving parts and lower energy prices. However, the environmental footprint of electric vehicle production, especially battery manufacturing, remains a major concern. Mining for lithium, cobalt, and nickel is associated with ecological degradation, water resource strain, and socio-economic tensions in producing countries [11]. Furthermore, expanding electric vehicle adoption requires substantial investment in charging infrastructure and grid upgrades, with cost and deployment pace varying widely between regions [12]. Additional challenges include battery recycling, limited range, and longer charging times relative to internal combustion engine vehicles, though rapid progress in solid-state battery technologies and vehicle-to-grid systems may mitigate these issues over time [13]. Overall, electric vehicles represent a highly effective long-term solution for decarbonising road passenger transport, but their limitations highlight the need for complementary strategies. In sectors such as aviation, shipping, and heavy-duty freight, as well as in the near term while charging infrastructure and new fleets are deployed, alternative low-carbon fuels and bridging technologies compatible with existing infrastructure will be essential to achieving immediate emissions reductions.

1.3.2 Hydrogen and Hydrogen Fuel Cells

Hydrogen fuel cell vehicles are especially suited to decarbonising heavy-duty, high-utilisation, and long-distance transport applications due to their fast refuelling times and high

energy density. These vehicles emit only water vapour during operation and, when powered by green hydrogen, offer a pathway to near-zero emissions transport. However, today's hydrogen is predominantly produced via fossil fuels (grey hydrogen), with significant associated greenhouse gas emissions, undermining its environmental benefits [14, 15]. Transitioning to green hydrogen through electrolysis requires vast renewable electricity inputs and poses scalability and economic challenges. Furthermore, the hydrogen economy faces immense capital hurdles: building out the full supply chain, including electrolysis plants, high-pressure storage, distribution networks, and fuelling stations, demands coordinated infrastructure investment on a massive scale [16]. The use of rare and costly materials such as platinum in fuel cells, along with public concerns over hydrogen safety and storage, further complicate deployment. In comparison to battery electric vehicles, hydrogen fuel cell vehicles also have lower well-to-wheel efficiency, due to conversion and compression/liquefaction losses, which may limit their competitiveness in certain markets [17]. While hydrogen has clear potential in the long term for decarbonising heavy-duty freight, shipping, and aviation, its reliance on large-scale renewable inputs and costly new infrastructure means it is unlikely to provide near-term emissions reductions across the wider transport sector. Here, advanced biofuels compatible with existing diesel and petrol infrastructure offer a more immediate and scalable pathway, bridging the gap until hydrogen technologies can mature and be deployed at meaningful scale.

1.3.3 Other Options

Beyond electric vehicles and hydrogen, a range of complementary approaches contribute to transport decarbonisation. Synthetic fuels (e-fuels), made from green hydrogen and captured CO₂, are being developed as drop-in replacements for conventional fuels, leveraging existing infrastructure and engines; however, their production is highly energy-intensive and inefficient compared to direct electrification [18]. Ammonia is also under evaluation, particularly for shipping, due to its carbon-free combustion potential and existing global transport network, though it presents challenges related to nitrogen oxides (NO_x) emissions and toxicity [19]. More immediately impactful are modal shifts toward public transport, active mobility (e.g., cycling and walking), and compact urban design, which can substantially reduce emissions, congestion, and energy demand [20, 21]. These strategies

require investment in infrastructure and policy frameworks to incentivise behaviour change but are essential to creating sustainable, multimodal transport systems.

1.3.4 Biofuels as an Immediate Solution for Transport Decarbonisation

Biofuels represent one of the most viable near-term solutions for reducing greenhouse gas emissions in the transport sector, particularly in modes where electrification is not yet feasible. A key advantage of biofuels lies in their compatibility with existing internal combustion engines and refuelling infrastructure. Unlike many low-carbon alternatives, biofuels can be blended with or directly substitute for conventional gasoline, diesel, and jet fuel, enabling rapid deployment without the need for costly new vehicle technologies or supply chains.

First-generation biofuels, such as ethanol from sugarcane and maize or biodiesel from soybean and palm oil, are already widely adopted. However, their use raises sustainability concerns due to indirect land-use change, biodiversity loss, and competition with food production [22]. These challenges have catalysed a transition towards more sustainable alternatives: second- and third-generation biofuels, often referred to collectively as advanced biofuels. These fuels are produced from non-food biomass such as agricultural residues (e.g., wheat straw, corn stover), lignocellulosic feedstocks (e.g., switchgrass, wood chips), organic waste, and algae. They offer significantly lower lifecycle greenhouse gas emissions, up to 85–90% reductions compared to fossil fuels, without competing with food supply chains or triggering large-scale deforestation [23, 24].

Advanced biofuels are particularly critical for hard-to-electrify segments like aviation, maritime shipping, and heavy-duty freight, where high energy density and long refuelling intervals are essential. Technologies such as hydrotreated vegetable oils (HVO), Fischer–Tropsch fuels, and alcohol-to-jet (ATJ) pathways are progressing toward commercial viability. In the aviation sector, sustainable aviation fuels (SAFs) derived from these processes have already been certified under the American Society for Testing and Materials (ASTM) standards for blending up to 50% with conventional kerosene, and full drop-in fuels are under development [25].

Despite their promise, advanced biofuels face a number of technical and economic barriers. Feedstock availability remains limited and regionally variable, while bioconversion technologies are capital-intensive and not yet scaled to match fossil fuel volumes. Moreover, the development of integrated supply chains, linking sustainable biomass production with reliable collection, transport, and biorefinery capacity, requires substantial public and private investment. Production costs for advanced biofuels remain higher than fossil-based fuels, though techno-economic analyses suggest that continued research and development and policy support could make them cost-competitive within the decade [26].

To unlock the full potential of biofuels in decarbonising transport, strong policy frameworks are essential. These include mandates for low-carbon fuel standards, subsidies for sustainable feedstock cultivation, investment in biorefinery infrastructure, and clear sustainability criteria to prevent adverse land-use impacts. The EU's Renewable Energy Directive, for instance, sets limits on first-generation biofuels and promotes the uptake of advanced alternatives through a defined list of eligible feedstocks and double-counting mechanisms [27]. Similar initiatives are emerging globally, underlining the strategic importance of biofuels as a bridging technology in the transition to net-zero transport.

In summary, advanced biofuels offer an immediately deployable and infrastructure-compatible solution for reducing transport emissions, particularly in sectors where electrification is constrained. While technical and economic challenges remain, ongoing innovation and supportive policy environments are key to realising their full potential in a sustainable and equitable energy transition.

1.4 Legislation for Biofuels

1.4.1 Renewable Energy Directives I, II & III

The European Union's Renewable Energy Directive (RED I), enacted in 2009, set a binding target requiring that 10% of energy consumed in the transport sector originate from renewable sources by 2020 [28]. While this initiative aimed to reduce greenhouse gas emissions and promote energy diversification, it inadvertently led to significant issues. The emphasis on first-generation biofuels, derived from food and feed crops, intensified the "food vs. fuel" debate, as agricultural lands were increasingly used for biofuel production,

potentially impacting food prices and security. Additionally, the heightened demand for biofuel feedstocks contributed to indirect land-use changes, such as deforestation, which undermined the environmental objectives of the directive.

In response to these challenges, the European Commission introduced the recast Renewable Energy Directive (RED II) in 2018, emphasising sustainability and the advancement of biofuels not derived from food crops. RED II mandates that by 2030, 14% of the energy consumed in the transport sector must come from renewable sources [27]. Within this framework, there is a specific focus on advanced biofuels produced from feedstocks listed in Part A of Annex IX. The directive sets progressive sub-targets for these advanced biofuels: at least 0.2% of transport energy consumption by 2022, increasing to 1% by 2025, and reaching at least 3.5% by 2030. Conversely, biofuels produced from feedstocks listed in Part B of Annex IX, such as used cooking oil and certain animal fats, are capped at contributing no more than 1.7% to the transport energy mix by 2030 [27]. These legislative measures underscore the EU's commitment to mitigating the adverse effects associated with conventional biofuels and highlight the necessity of transitioning to advanced biofuels. Derived from non-food-based feedstocks, including agricultural residues and waste materials, advanced biofuels offer a more sustainable alternative, minimising competition with food production and reducing the risk of indirect land use change.

The most recent revision, RED III, entered into force in 2023 as part of the EU's "Fit for 55" package, raising ambition beyond RED II. It increases the transport sector target by requiring a 14.5% reduction in greenhouse gas intensity or a 29% share of renewables in final energy consumption by 2030, providing Member States flexibility in how they meet the goal. Importantly, RED III introduces a combined 5.5% sub-target for advanced biofuels (Annex IX Part A) and renewable fuels of non-biological origin (RFNBOs) in transport, of which at least 1% must be RFNBOs by 2030 [29]. The directive strengthens sustainability criteria, increases minimum greenhouse gas saving thresholds for biofuels, and expands traceability requirements through the EU Biofuels Database, making reporting and verification more rigorous. It also tightens rules on high indirect land-use change risk feedstocks, reinforces caps on certain Annex IX Part B materials, and extends monitoring of feedstock availability. Collectively, RED III consolidates the EU's transition away from food-based biofuels and toward advanced and synthetic alternatives, while recognising the

role of biofuels compatible with existing infrastructure in securing near-term emissions reductions.

1.4.2 Ireland's Climate Action Plan 2024

Ireland's Climate Action Plan 2024 (CAP24) sets out an ambitious roadmap for reducing greenhouse gas emissions across all sectors, in line with the legally binding target of a 51% reduction in national emissions by 2030 and achieving net-zero by 2050. The transport sector, currently responsible for approximately 18% of Ireland's emissions, is a critical focus, with a specific goal of cutting emissions in this sector by 50% by 2030 [30]. This reduction is to be achieved through a combination of behavioural, infrastructural, and technological changes, underpinned by the "Avoid-Shift-Improve" framework.

The strategy to decarbonise transport rests on three pillars. First, "Avoid" measures aim to reduce the need for travel, particularly by supporting remote and hybrid work, improving digital connectivity, and promoting compact urban development. Second, "Shift" focuses on encouraging people to move from private vehicles to public or active modes of transport. This includes investment in rail, bus, and cycling infrastructure, reallocation of road space, and the expansion of public transport networks. Third, the "Improve" pillar focuses on enhancing the energy efficiency of vehicles by accelerating electric vehicle adoption and rolling out nationwide charging infrastructure, as well as supporting low-emission fuels and technologies for heavy-duty and long-distance applications.

Key targets include reducing fuel usage in transport by 50%, increasing the number of daily public transport journeys by 130%, boosting active travel (walking and cycling) journeys by 50%, and cutting daily private car journeys by 25% by 2030. To support the transition to lower-emission vehicles, the plan aims for 175,000 passenger electric vehicles on the roads by 2025, with continued acceleration thereafter. CAP24 also proposes enabling systemic change through integrated spatial and transport planning, tighter management of road infrastructure (such as speed limits and parking reforms), and the potential introduction of low-emission zones. Collectively, these policies represent a decisive shift toward a more sustainable, efficient, and accessible transport system that supports Ireland's long-term climate goals [30].

1.4.2.1 Biofuels in Ireland's Climate Action Plan 2024

Ireland's Climate Action Plan 2024 recognises biofuels, particularly advanced biofuels, as an essential component of the country's strategy to decarbonise the transport sector, especially for applications where electrification is less feasible, such as heavy-duty vehicles, aviation, and maritime transport. While acknowledging that the electrification of passenger cars will play a leading role in reducing emissions, the Plan highlights that liquid biofuels remain necessary to meet the EU Renewable Energy Directive II (RED II) transport target of 14% renewables by 2030. In practice, this will require steadily increasing blending rates through the Biofuels Obligation Scheme, ensuring a clear and enforceable trajectory.

With the adoption of RED III, however, Ireland must now align not only with the 14% renewable share but also with the 5.5% combined advanced biofuel and RFNBO sub-target in transport, alongside the minimum 1% RFNBO requirement [29]. CAP24 therefore underscores the importance of shifting toward waste-derived, non-food-based advanced biofuels, in accordance with Annex IX, to avoid land-use conflicts and maximise greenhouse gas savings. It also commits to exploring opportunities for scaling up the production and use of advanced biofuels from agricultural residues, industrial wastes, and other sustainable feedstocks, supporting both emissions reduction and rural economic development. By integrating RED III requirements into national policy, Ireland aims to balance the near-term need for diesel- and petrol-compatible low-carbon fuels with the longer-term transition toward electrification, hydrogen, and other zero-emission solutions.

1.5 Lignocellulosic Biomass

Lignocellulosic biomass represents the most abundant renewable organic carbon source on Earth and has gained increasing attention as a sustainable feedstock for advanced biofuel production [31]. It consists primarily of cellulose (30–45%), hemicellulose (20–35%), and lignin (10–25%), alongside smaller fractions of ash, extractives, and other minor components. The structural polysaccharides, cellulose and hemicellulose, provide a rich source of relatively energy dense carbohydrates, while lignin imparts recalcitrance but also potential as a source of aromatic platform molecules.

Within the European Union, over 900 million tonnes of agricultural residues are generated annually, of which wheat straw and corn residues are among the most abundant fractions [32, 33]. In Ireland, the potential for lignocellulosic biomass utilisation is similarly significant, with wheat straw alone representing a major underutilised residue stream from cereal production [34]. Despite their classification as waste under the EU Waste Framework Directive, these materials represent valuable secondary resources that can be channelled into the bioeconomy. The high carbohydrate fraction of lignocellulosic biomass is of particular interest for the production of advanced biofuels, such as alkyl levulinates, ethanol, and sustainable aviation fuels, through hydrolysis, alcoholysis, and catalytic upgrading pathways [35]. By converting these residues into high-value energy carriers, their utilisation not only supports waste minimisation but also aligns with EU directives on renewable energy and decarbonisation of transport.

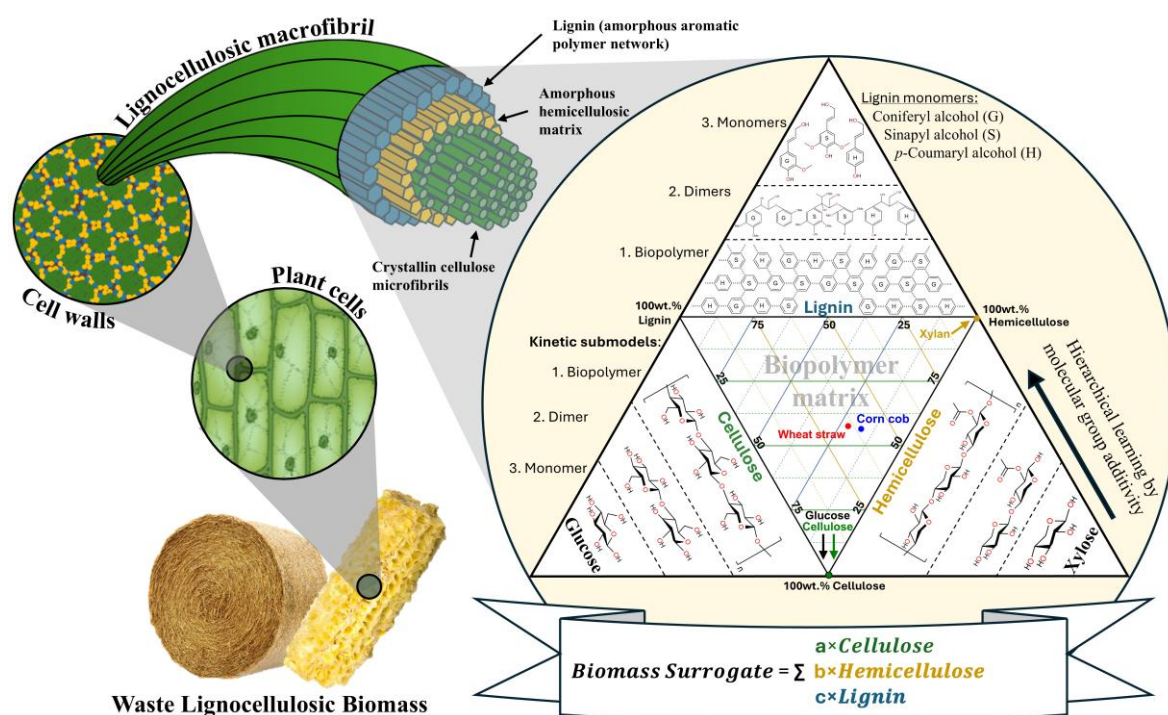


Figure 4. Composition of lignocellulosic biomass, showing the hierarchical organisation of cellulose, hemicellulose, and lignin from the plant cell wall to the macrofibril scale. Representative monomers for each fraction are depicted, alongside a ternary diagram illustrating the variable proportions of cellulose, hemicellulose, and lignin across different biomass feedstocks.

Thus, lignocellulosic biomass, with its abundance, waste designation, and favourable carbohydrate composition, offers an immediate and strategic route for advanced biofuel production in Ireland and across the EU. Beyond its value as a feedstock, its well-defined composition of cellulose, hemicellulose, and lignin also lends itself to surrogate analysis and

hierarchical modelling approaches. As illustrated in Figure 4, these biopolymers can be decomposed into repeating structural units, glucose, xylose, and phenylpropanoid monomers, allowing models to capture fundamental reaction behaviour at the subunit level. By training models on the reactivity of these simpler constituents, hierarchical learning provides a route to predict the behaviour of intact, heterogeneous biomass during catalytic conversion. This thesis therefore investigates not only the valorisation of lignocellulosic residues into advanced biofuels, but also the development of modelling strategies that link molecular-scale chemistry with bulk process performance.

1.6 Alcoholysis of Lignocellulosic Biomass to Alkyl Levulinates

Alcoholysis of lignocellulosic biomass is emerging as a highly promising route for producing alkyl levulinates, which are energy-dense, oxygenated fuel additives compatible with petrol and diesel engines. The process is inherently simple, requiring only the reaction of biomass with an alcohol, typically ethanol or butanol, in the presence of an acid catalyst. The operational simplicity of this single-pot process eliminates the need for multiple separation and purification steps, making it suitable for industrial integration with minimal technological barriers [36].

A recent techno-economic analysis by Silva et al. assessed 148 process scenarios and identified 53 as commercially promising for producing ethyl levulinate and found that every one of them used sulphuric acid (H_2SO_4) as the catalyst [37]. While there has been significant research into more selective or heterogeneous alternatives, sulphuric acid remains the only catalyst capable of achieving maximum yields while keeping operational costs low. Its widespread availability and low price make it the most economically viable option at present.

Cost analysis of these alcoholysis processes also highlights their economic strengths. On average, the cost of alcohol accounts for 38% and the cost of lignocellulosic biomass for 34% of the total production cost [37]. Ethanol is typically preferred over alternatives like biobutanol due to its lower price and higher market availability [38]. Feedstocks such as wheat straw are particularly attractive because of their abundance, low cost, low moisture content, and existing collection infrastructure. These attributes reduce both logistical complexity and cost, supporting the scalability of the process.

Efficiency is another strength of alcoholysis. Ethyl levulinate yields are consistently high when using sulphuric acid and optimised reaction conditions, often exceeding 50 wt% based on the carbohydrate content of the biomass [35, 39]. These yields, combined with the use of low-cost inputs and mild reaction conditions, make alcoholysis a cost-effective and scalable method for producing advanced biofuels compatible with existing fuel infrastructure.

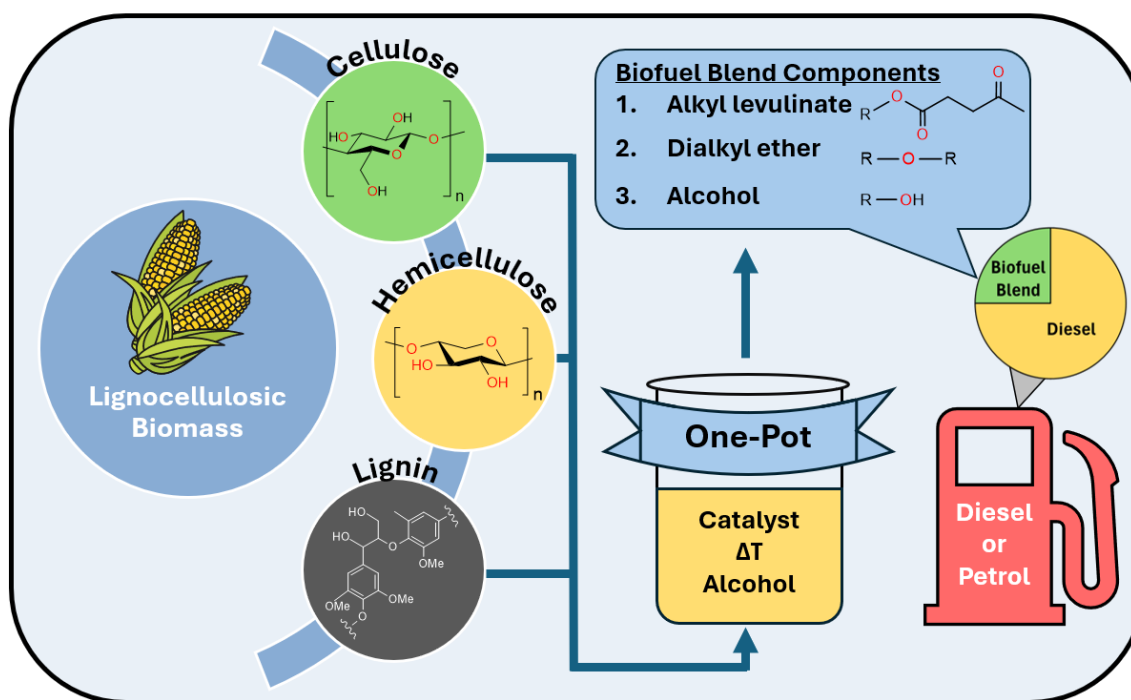


Figure 5. Conceptual framework of the surrogate approach applied to the alcoholysis process for producing three-component advanced biofuel blends suitable for diesel and petrol applications.

1.7 Potential for Three-Component Advanced Biofuel Blends

Advanced biofuels derived from lignocellulosic feedstocks represent a promising pathway for displacing fossil-derived diesel in compression ignition engines. One particularly attractive route is the acid-catalysed alcoholysis of biomass, which yields a product mixture primarily comprised of an alkyl levulinate, the alcohol solvent employed, and the corresponding dialkyl ether. This mixture is advantageous because each constituent plays a complementary role: the alkyl levulinate fraction acts as the principal oxygenated energy carrier, the dialkyl ether provides a high-cetane, low-sooting ignition enhancer, and the alcohol contributes volatility control and blend homogeneity, while also reducing particulate emissions through its oxygenate content [40].

Recent studies have demonstrated that these ternary blends can be tailored to meet diesel fuel property specifications, including density, viscosity, and flash point. In particular, Wiseman et al. [41] showed that maintaining alkyl levulinate as the dominant component (≥ 50 vol%) allows the formulation of stable blends compliant with European diesel fuel standard, EN 590 standards. Using a design-of-experiments approach, predictive models for physical properties such as flash point and kinematic viscosity were generated with an average relative deviation below 5%, indicating the reliability of this approach for blend optimisation [41].

Beyond physical properties, combustion behaviour is strongly influenced by blend composition. Michelbach et al. [42] highlighted that ignition delay times and heat release rates can be tuned by altering the relative proportions of the three components, providing valuable control over engine performance. When tested in diesel engines, butyl- and pentyl-based blends in particular demonstrated stable operation with reductions in particulate matter and volatile organic compound emissions relative to ultra-low sulphur diesel [41].

In addition, broader reviews emphasise that the three-component approach offers clear synergistic benefits: because the mixture is produced directly from alcoholysis, there is no need for extensive downstream separation, and the same feedstock and process can generate fuels compatible with both gasoline and diesel applications depending on composition. This flexibility represents a significant advantage over binary blends or single-component biofuels [43].

The work reported here formed part of the Sustainable Liquid Advanced Biofuels from Biomass (SusLABB) project (EPSRC-SFI EP/T033088/1), a collaborative programme between Trinity College Dublin and the University of Leeds, with additional international and industrial partners. The overarching aim of SusLABB was to develop methodologies for producing tailored, multi-component biofuel blends directly from lignocellulosic feedstocks, optimising both the synthetic process and final fuel compositions for technical, economic, and environmental performance. Within this framework, my research contributed to Work Packages 1 and 2 (Feedstock Preparation and Characterisation, and Fuel Production), while subsequent work packages at Leeds examined physical property testing, engine and emissions performance, and techno-economic–sustainability analysis (Figure 6). The SusLABB concept explicitly emphasises the production of biofuel blends in situ, avoiding

costly separation steps, and enabling the direct generation of drop-in fuels with specified combustion properties.

Taken together, these findings demonstrate that ternary blends of alkyl levulinates, alcohols, and dialkyl ethers are a highly versatile class of advanced biofuels. Their favourable combination of physical, combustion, and blending properties, coupled with their origin in waste lignocellulosic feedstocks, makes them particularly promising candidates for drop-in diesel replacement.

Sustainable Liquid Advanced Biofuels from Biomass Project (SusLABB)

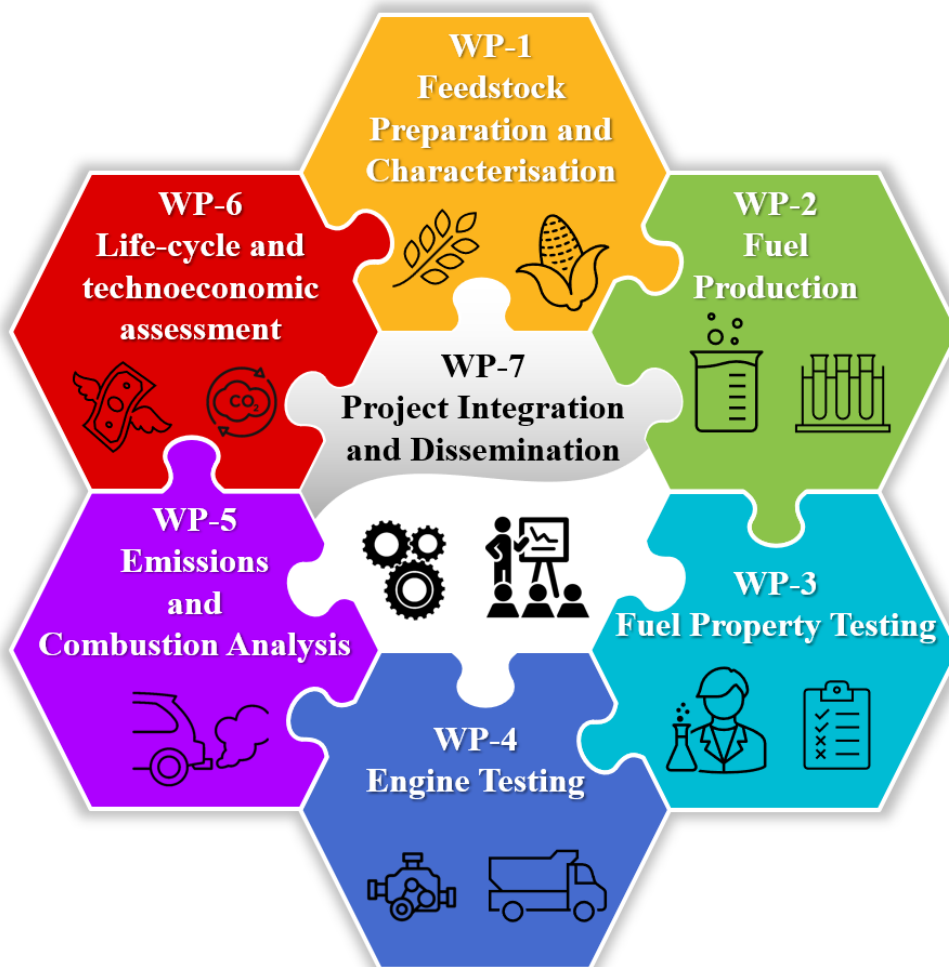


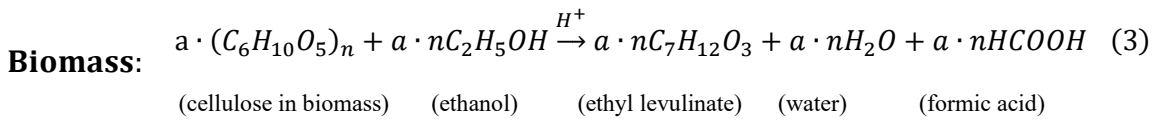
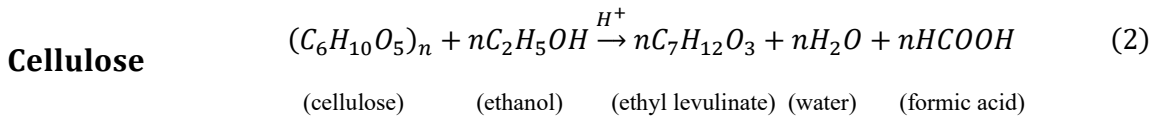
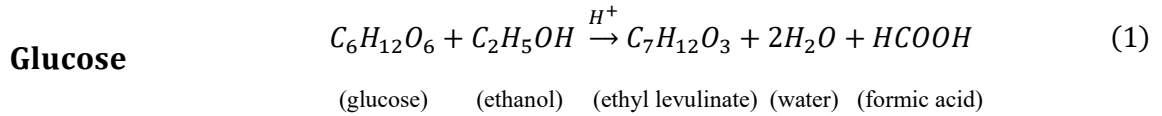
Figure 6. Schematic overview of the Sustainable Liquid Advanced Biofuels from Biomass (SusLABB) project, illustrating the seven interconnected work packages (WP1–WP7). The project spans feedstock preparation and characterisation and fuel production.

1.8 Alcoholysis Theory

1.8.1 Alkyl Levulinate Formation

Alkyl levulinates are produced via the acid-catalysed alcoholysis of hexose carbohydrates, such as glucose, in the presence of a lower alcohol (Equations 1-3). The transformation proceeds through proton-mediated pathways in which the carbohydrate is converted to the corresponding alkyl levulinate, accompanied by the formation of two equivalents of water and one equivalent of formic acid. The latter may undergo further esterification with the alcohol to generate the corresponding alkyl formate and an additional molecule of water. While the formal mechanism suggests that the hydrogen ion is regenerated in each catalytic cycle, in practice, side reactions involving lignocellulosic feedstocks partially consume the catalyst, thereby reducing the effective proton concentration available for the main transformation [44]. These competitive processes are considered in detail in Chapters 5 and 6.

The overall stoichiometry of the acid-catalysed alcoholysis reactions for glucose, cellulose, and lignocellulosic biomass (exemplified here by corn cob) can be generalised as follows [44]:



where a is the mass fraction of cellulose in the corn cob sample.

1.8.2 Dialkyl Ether Formation

Dialkyl ethers are well-documented by-products of acid-catalysed alcoholysis reactions [45]. These compounds are generated through the proton-mediated dehydration of two alcohol molecules, producing one equivalent of water as a by-product (Figure 7). Although typically regarded as an undesirable side reaction that consumes alcohol feedstock, their formation is often overlooked in experimental studies.

Notably, Mascal et al. reported that up to 67 mol% of ethanol was converted to diethyl ether during the reaction of dried conifer wood with 2-naphthalenesulfonic acid at 200 °C, over 4 hours [46]. The economic impact of such side reactions is significant, as Silva et al. demonstrated that alcohol contributes approximately 38% of the total production cost in ethyl levulinate synthesis from lignocellulosic biomass [37]. Accordingly, minimising alcohol losses to etherification is essential to improving the techno-economic feasibility of the process.

Strategies to suppress ether formation include the use of reduced acid concentrations, as suggested by Mascal and further verified by Zhu [47]. However, this approach is accompanied by a concomitant decrease in the rate of ethyl levulinate production. This trade-off highlights the need for a balanced catalytic environment that mitigates dialkyl ether formation while maintaining efficient levulinate yields.

Despite the clear relevance of this side reaction, quantitative determination of dialkyl ether concentrations is rarely performed. Without such data, accurate assessment of overall process efficiency and techno-economic viability remains incomplete. Careful evaluation of diethyl ether formation, particularly its rate relative to that of ethyl levulinate, is therefore critical to the rational design and optimisation of biomass alcoholysis processes.

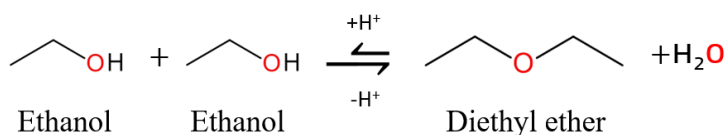


Figure 7. Proposed reaction scheme for the acid catalysed formation of diethyl ether from two molecules of ethanol.

1.8.3 Humin Formation

The hydrothermal and solvothermal conversion of carbohydrates is frequently accompanied by the formation of insoluble, carbonaceous polymeric by-products collectively referred to as humins [48, 49]. These heterogeneous solids are generally believed to originate from reactive carbonyl intermediates, such as aldehydes and ketones, which arise from the partial decomposition of the carbohydrate feedstock (Figure 8). Subsequent condensation and polymerisation of these intermediates yield the highly cross-linked and structurally complex humin material.

Recent studies have highlighted the influence of solvent environment on humin formation. For instance, Shi et al. reported that no detectable humins were produced during the reaction of glucose in ethanol, whereas in water and tetrahydrofuran (THF), 61% and 53% of the initial carbon, respectively, was converted into humins [48]. This inhibition has been attributed to the preferential reaction of aldehydes and ketones with alcohol molecules, thereby suppressing their self-condensation and polymerisation into humins [50].

From a process optimisation perspective, humin formation is of considerable importance. Although generally treated as an unavoidable by-product, humins represent a significant sink for carbon and, consequently, a loss in alkyl levulinate yield. Furthermore, they complicate reaction handling, separation, and catalyst recovery. Given these impacts, careful assessment of humin formation is essential not only for mechanistic understanding but also for evaluating the overall techno-economic feasibility of biomass alcoholysis processes.



Figure 8. Proposed reaction scheme for the formation of humins from lignocellulosic biomass.

1.8.4 Water Formation

All the pathways discussed above, namely, the formation of alkyl levulinates, dialkyl ethers, and humins, generate water as a stoichiometric co-product (Equations 1-3, Figure 7 and 8). Consequently, water is inevitably present in the reaction medium, often in appreciable quantities.

The presence of water is significant for two principal reasons. First, the esterification step that produces alkyl levulinates is an equilibrium-limited process [37]. Accumulated water therefore suppresses forward esterification and reduces levulinate yields, with additional contributions arising from etherification and humin formation. Second, from a practical standpoint, water removal is necessary before the reaction mixture can be employed directly as a fuel or blended into fuel formulations. The energy and processing costs associated with dehydration add further weight to the techno-economic implications of water generation.

While the present work does not explicitly address post-reaction water management, it is clear that minimising secondary reactions that contribute additional water is essential for both process efficiency and commercial viability.

1.9 Kinetic Modelling for Biomass Alcoholysis

This work sets out to develop a detailed mechanistic and kinetic description of the acid catalysed conversion of lignocellulose-derived carbohydrates in alcohol solvents to advanced biofuel components. A complete understanding of this chemistry cannot be achieved solely by experiment, as experimental observations capture only a subset of intermediates and products, nor solely by theoretical calculation, which is challenged by the compositional and solvent complexity of biomass alcoholysis. Instead, the integration of both, mediated through the construction of kinetic models, offers the opportunity to interrogate reaction systems at a fundamental molecular level. In this thesis, hierarchical surrogate biochemical kinetic models are developed and applied to the ethanolysis and butanolysis of lignocellulosic biomass. By embedding these models within a framework that couples time-resolved measurements, theoretical insights, and machine-learned optimisation, the work extends earlier ethanolysis modelling [51] and recent experimental–theoretical mechanistic studies [52] to achieve new depth of understanding of alcoholysis chemistry.

A defining feature of this work is the mechanistic parsimony of the surrogate kinetic models. For glucose and cellulose ethanolysis, ethyl glucoside is represented as the sole intermediate en route to ethyl levulinate. This choice is not arbitrary: experimental studies have shown that, under acid catalysed ethanolysis conditions, the dominant carbon flux

proceeds via ethyl glucoside, with negligible formation of fructose, hydroxymethylfurfural (HMF), or ethoxymethylfurfural (EMF) [51]. This pathway is mechanistically distinct from fructose ethanolysis, where furanic intermediates play a central role. Consequently, the simplified surrogate scheme reflects the experimentally observed selectivity of glucose and cellulose ethanolysis, ensuring both mechanistic fidelity and tractability of parameter estimation.

Through this combination of mechanistic reduction grounded in experiment and catalytic representation grounded in theory, the surrogate kinetic models developed herein provide a robust platform for dissecting the chemistry of biomass alcoholysis and guiding the design of advanced biofuel production processes.

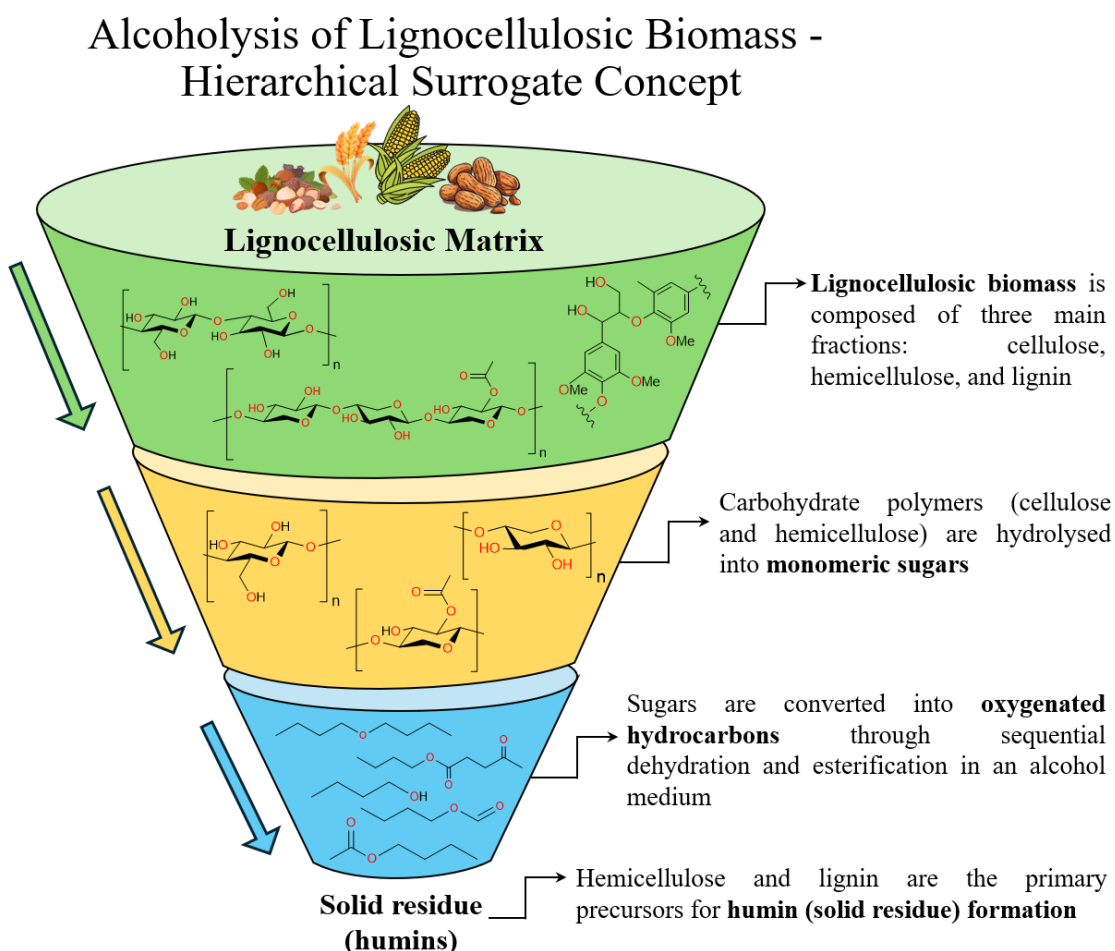


Figure 9. Conceptual framework employing surrogate and hierarchical learning through molecular group additivity principles to predict product distributions (butanolysis products shown) from biomass conversion based on feedstock composition.

1.9.1 Fundamental Theory

Theoretical chemistry provides indispensable insight into the thermodynamics and kinetics of the elementary steps that underpin biomass alcoholysis. Acid catalysed pathways proceed through protonation of glycosidic bonds, cleavage to oxocarbenium ions, and nucleophilic attack by solvent molecules. The active catalytic species in alcohol solvents is not the free proton but the protonated alcohol, $[\text{ROH}_2]^+$, which forms through preferential solvation of H^+ by the solvent. Computational studies have shown that this species is the dominant proton carrier in alcohol media, lowering energy barriers for dehydration and etherification reactions and altering hydrogen transfer mechanisms in ways that promote product selectivity [53].

In ethanolysis of glucose, the preferred mechanistic route involves substitution at the C1 hydroxyl position to yield ethyl glucoside. Quantum chemical calculations confirm that this pathway proceeds with an activation barrier comparable to glucose–fructose isomerisation, while experimental data demonstrate that fructose and furanic intermediates are not significant in glucose or cellulose ethanolysis [51]. This establishes ethyl glucoside as the principal kinetic intermediate and validates its inclusion as the sole pathway intermediate in the surrogate model.

1.9.2 Experimental Measurements

Experimental datasets provide the essential basis against which kinetic models are calibrated and validated. For alcoholysis systems, time-resolved measurements of species concentrations are obtained under varied temperature, catalyst concentration, and solvent conditions. These datasets capture the evolution of stable products such as alkyl levulinates, ethers, and secondary esters, and reveal the characteristic timescales of carbohydrate conversion.

In addition to capturing transient and endpoint behaviour, steady-state yields for levulinate production were specifically targeted. These plateaus represent time-invariant (‘steady-state’) compositions under the studied conditions and may approach the thermodynamic limit for the measured liquid-phase products, though continued humin formation can keep the full system from strict equilibrium. By constraining the models to

reproduce these steady-state maxima, the framework ensures that predictions are not only kinetically plausible but also consistent with the observed steady-state behaviour and plausible thermodynamic tendencies for the liquid phase. In this way, the models are designed to replicate and predict maximum achievable levulinate yields under the studied conditions.

By-products, including insoluble humins and soluble unknowns, are typically quantified indirectly through elemental analysis or carbon balance closure. Transient species such as oxocarbenium ions or protonated alcohols cannot be observed directly but must be inferred from mechanistic interpretation and theoretical studies [52, 53]. Thus, experimental evidence both constrains and motivates surrogate modelling: the data establish which intermediates are kinetically relevant and which must be excluded for reasons of parsimony, while also defining the observable envelopes that models must reproduce.

When integrated with theoretical chemistry, these experimental measurements form the physical anchor of the hierarchical surrogate framework, ensuring that the resulting models are empirically constrained, chemically realistic, and predictive across different substrates and conditions. [51, 54].

1.9.3 Hierarchical Surrogate Biochemical Kinetic Modelling

Kinetic modelling provides a structured means to interrogate mechanistic hypotheses, particularly in systems where many intermediates are transient or experimentally inaccessible. In this work, a hierarchical surrogate biochemical kinetic modelling framework was developed for the sulphuric acid catalysed ethanolysis and butanolysis of lignocellulosic biomass. The framework proceeds in a stepwise fashion from simple substrates (glucose) to increasingly complex ones (cellulose, xylan, and real lignocellulosic feedstocks), with each sub-model parameterised and validated before extension to the next level. This progression ensures mechanistic self-consistency, prevents overfitting, and allows clear attribution of kinetic parameters to specific substrate classes [51, 54, 55].

A central principle of this surrogate approach is mechanistic parsimony. For glucose and cellulose ethanolysis, the models include ethyl glucoside as the sole intermediate en route to ethyl levulinate. This simplification is strongly supported by experimental data, which show

that ethyl glucoside accumulates as the major reaction intermediate, while fructose, hydroxymethylfurfural, or ethoxymethylfurfural are either undetected or present in trace yields under comparable conditions [51]. Thus, while fructose and furanic pathways dominate in fructose ethanolysis, they are not kinetically relevant for glucose or cellulose, and their omission from the model improves parameter tractability without loss of mechanistic fidelity.

The models also explicitly represent the catalytically active species as the protonated alcohol $[\text{ROH}_2]^+$, following both theoretical and experimental evidence that proton solvation by alcohol enhances reactivity relative to free protons [52, 53]. Incorporating this mechanistic detail is essential for reproducing solvent promotion effects and achieving chemical consistency across ethanolysis and butanolysis systems.

Parallel to substrate progression, a biochemical surrogate compositional model represents lignocellulose as cellulose, hemicellulose, and a non-carbohydrate “remaining mass” fraction, bridging complex feedstocks with the well-characterised reactivity of mono- and polysaccharides [54, 56, 57]. By systematically embedding these surrogate representations within the hierarchical framework, the modelling captures both the observable outcomes and the underlying chemistry of biomass alcoholysis, offering predictive insight into advanced biofuel formation pathways.

1.9.4 Ethanolysis and Butanolysis Models

The surrogate kinetic models developed in this work focus on the acid catalysed ethanolysis and butanolysis of glucose and cellulose, extended to lignocellulosic feedstocks. Their purpose is to capture the conversion of carbohydrate substrates to alkyl levulinates alongside parallel solvent dehydration to dialkyl ethers. By limiting the models to the principal observed pathways while incorporating by-product formation in a lumped fashion, the framework remains mechanistically faithful yet sufficiently compact for predictive analysis.

For ethanolysis, experiments were first performed to establish the simplified mechanistic scheme [44]. Ethyl glucoside was taken as the sole intermediate en route to ethyl levulinate, consistent with experimental evidence of its accumulation in glucose and cellulose

ethanolysis. The model also incorporates ethanol dehydration to diethyl ether and lumped by-product channels. In particular, insoluble humins and soluble unknowns are represented as distinct sinks of carbon: humins correspond to the solid residue isolated experimentally, while soluble unknowns are inferred by mass closure. This treatment ensures that the models replicate the experimentally observed steady-state yields, thereby capturing both kinetic behaviour and maximum achievable levulinate concentrations.

Building on the ethanolysis framework, the butanolysis model was developed to account for additional product channels identified experimentally. Alongside the formation of *n*-butyl levulinate and di-*n*-butyl ether, secondary esterification reactions with formic acid and acetyl substituents were included to represent the observed formation of *n*-butyl formate and *n*-butyl acetate [58-60]. The separation of humins from soluble unknowns was maintained, but the butanolysis scheme also incorporated hemicellulose-derived furfural and its subsequent condensation into humins, in line with experimental quantification [61-63].

Finally, for lignocellulosic feedstocks such as corn cob, the surrogate model decomposes the composition into cellulose, hemicellulose, and a lignin-containing “remaining mass” fraction. Each of these fractions contributes to alkyl levulinate production and by-product formation through the pathways established for simpler substrates. In this way, the ethanolysis and butanolysis models provide a coherent and scalable representation of biomass alcoholysis, linking controlled experiments on model substrates with the complexity of real feedstocks

1.9.5 Model Calibration and Machine-Learned Optimisation

Robust parameterisation is essential for predictive modelling. Here, calibration was achieved by a hierarchical optimisation strategy, in which parameters determined for simple substrates were fixed at higher levels of complexity. Optimisation employed the Machine Learned Optimisation of Chemical Kinetics (MLOCK) framework [55], which iteratively refines Arrhenius parameter bounds by generating and evaluating extensive candidate model libraries. Genetic seed scans identify optimal parameter sets that reproduce experimental profiles across temperature and composition ranges.

This combination of mechanistic modelling and machine learning represents a significant advance over empirical solution-phase kinetic models [64, 65]. By embedding mechanistic elementary steps informed by theory, experimental observations, and machine-learned parameterisation, the approach yields predictive, chemically consistent models spanning glucose to lignocellulose.

1.10 Summary and Implications

Transport remains one of the most challenging sectors to decarbonise, particularly in aviation, shipping, and heavy freight where electrification is not yet feasible. While electric vehicles and hydrogen technologies will play increasing roles in the long term, advanced biofuels offer an immediate and scalable solution that is compatible with existing engines and infrastructure. This thesis therefore concentrates on the alcoholysis of lignocellulosic biomass and the development of surrogate kinetic models to enable the production of tailored, multi-component drop-in fuels, providing a practical pathway for near-term emissions reductions in the transport sector.

Chapter 2

Literature Review of Alcoholysis

2.1 Biomass Valorisation Pathways and the Role of Alcoholysis

The sustainable conversion of lignocellulosic biomass into fuels and chemicals has been widely investigated through a variety of thermochemical and catalytic routes. Among these, hydrolysis and hydrothermal liquefaction convert carbohydrates into platform molecules such as levulinic acid, hydroxymethylfurfural, and sugars in aqueous media [66]. Pyrolysis and catalytic fast pyrolysis enable rapid depolymerisation and deoxygenation, producing bio-oils rich in furans, phenolics, and hydrocarbons, though often requiring extensive upgrading due to instability and oxygen content [67]. Hydrogenolysis and hydrogenation routes are employed to convert levulinic acid and related intermediates into γ -valerolactone (GVL), alkanes, or polyols, but rely on external hydrogen sources and precious-metal catalysts [66].

Within this context, alcoholysis has emerged as a particularly attractive pathway. In alcoholysis, biomass-derived carbohydrates are converted in the presence of a Brønsted and/or Lewis acid catalyst and a lower alcohol solvent. The alcohol acts simultaneously as solvent, reactant, and stabilising agent, thereby preventing re-polymerisation and facilitating the one-pot conversion of carbohydrates into liquid biofuel precursors such as alkyl levulinates [66, 68, 69]. Reports have demonstrated that a wide range of sugars and biomass feedstocks undergo alcoholysis to form alkyl levulinates under moderate conditions (120–200 °C, 0.5–24 h) with examples using ethanol as the solvent, in the presence of a Brønsted and/or Lewis acid catalyst, including; glucose [58, 68–88], fructose [58, 68, 71, 72, 75–77, 81, 83, 85, 86, 88–97], sucrose [58, 68, 70, 74, 77, 81, 83, 86, 92, 94, 98], mannose [81],

maltose [81], inulin [58, 68, 74, 75, 81, 83, 85, 92], cellulose [50, 72, 74, 99-105], starch [75] and a range of biomasses [73, 106-118] which have been shown to form ethyl levulinate. Compared to aqueous hydrolysis, alcoholysis avoids extensive humin formation due to the stabilising effect of solvent participation, and compared to pyrolysis, it enables direct liquid-phase production of intermediates that are easily separated and upgraded [35, 66].

A further advantage of alcoholysis is the simplicity of the one-pot process. Unlike multistep hydrolysis–esterification approaches, alcoholysis directly yields alkyl levulinates without the need for isolation of levulinic acid intermediates [74]. This improves atom economy, reduces separations, and lowers the number of reaction steps, aligning with the principles of green chemistry [119]. Alcoholysis also allows for tuneable solvent–product systems, as the alcohol identity dictates the nature of the levulinate ester and the dialkyl ether by-product. This tunability creates opportunities for tailoring biofuel blends: ethanolysis produces ethyl levulinate and diethyl ether, while butanolysis yields *n*-butyl levulinate and di-*n*-butyl ether [35, 46, 120, 121]. These reaction pairs can serve as ternary blend components (levulinate ester + dialkyl ether + alcohol) that display synergistic properties when incorporated into petroleum fuels [40, 122].

The relevance of alkyl levulinates as advanced biofuels and additives is well established. Ethyl and *n*-butyl levulinate exhibit excellent miscibility with diesel and gasoline, improved lubricity, and enhanced combustion efficiency [35, 120]. Dialkyl ethers such as diethyl ether and di-*n*-butyl ether contribute high cetane numbers and clean combustion profiles [120]. Together with the unreacted alcohol, these components form stable ternary blends with promising application as drop-in biofuels [40, 42, 43, 122]. The strategic advantage of alcoholysis is therefore twofold: (i) it produces alkyl levulinates in a single step from abundant lignocellulosic feedstocks, and (ii) it generates dialkyl ether co-products that are themselves valuable blendstocks.

For these reasons, alcoholysis has become a focal pathway in biomass valorisation research. While hydrolysis, pyrolysis, and hydrogenolysis each offer unique advantages, alcoholysis uniquely combines simplicity, direct liquid production, solvent/reactant duality, and blendstock synergy, positioning it as one of the most promising technologies for the sustainable production of advanced biofuels.

2.2 Reaction Pathways and Side Products in Alcoholysis

The theoretical framework of alcoholysis has been outlined in Section 1.8, where the acid catalysed conversion of carbohydrates in alcohol solvents was described in terms of alkyl levulinate, dialkyl ether, water, and humin formation. This section reviews how these pathways are reported experimentally and how mechanistic studies have advanced their understanding.

2.2.1 Alkyl Levulinate Formation

The primary objective of alcoholysis is the formation of alkyl levulinates, which are obtained through multi-step dehydration and rearrangement pathways beginning with glucose or other polysaccharides. Under ethanolysis conditions reported in the broader literature, glucose first undergoes isomerisation to fructose, followed by successive dehydration to 5-hydroxymethylfurfural (HMF), which subsequently rehydrates to levulinic acid (LA) or directly esterifies to ethyl levulinate (EL) in ethanol-rich media [68, 69, 123, 124]. However, under the specific conditions studied in this work, the ethyl glucoside pathway predominates for glucose and cellulose conversion. In this route, glucose undergoes nucleophilic substitution at the anomeric carbon to form ethyl glucoside intermediates, which subsequently rearrange to ethyl levulinate. [51, 57]. Comparable steps occur in butanolysis, yielding *n*-butyl glucoside intermediates en route to *n*-butyl levulinate [120].

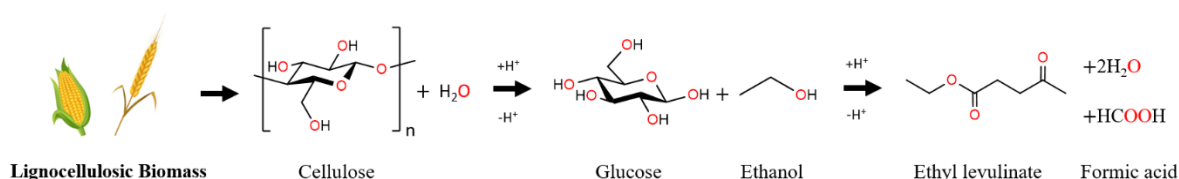


Figure 10. Proposed reaction scheme for the production of ethyl levulinate from lignocellulosic biomass [68].

Mechanistic studies combining experiment and theory have clarified the role of the alcohol solvent. Wang et al. [52] demonstrated that ethanol not only stabilises intermediates but also facilitates proton transfer by acting as a bridging molecule. These findings are consistent with observations of glucoside intermediates in experimental studies of both ethanolysis and butanolysis [44, 51, 57, 125].

2.2.2 Ether Formation

In addition to alkyl levulinates, alcoholysis inevitably produces dialkyl ethers through solvent dehydration. In ethanolysis, diethyl ether is formed via acid catalysed condensation of ethanol, a reversible process that consumes both solvent and protons [46, 61]. Similarly, butanolysis produces di-*n*-butyl ether through analogous acid catalysed etherification of *n*-butanol [120, 121]. Ether yields vary with reaction conditions, but their formation is unavoidable and has important implications for solvent balance, proton economy, and techno-economic analysis of alkyl levulinate production [46]. Despite this, many literature reports neglect ether quantification, representing a major knowledge gap in alcoholysis studies [44, 120].

2.2.3 Ester Co-products

Beyond alkyl levulinates and dialkyl ethers, alcoholysis also gives rise to secondary ester co-products formed through acid catalysed esterification reactions. The generation of formic acid during levulinate formation provides a mechanistic basis for the appearance of alkyl formates, such as ethyl formate in ethanolysis and *n*-butyl formate in butanolysis [44, 58, 68, 69]. Similarly, acetyl substituents present in hemicellulosic xylan may be released under reaction conditions, leading to the formation of acetate esters, most notably ethyl acetate and *n*-butyl acetate [63, 126, 127]. In addition, furfural, derived from the dehydration of xylose in hemicellulose, provides another mechanistic route to secondary products, where it can act as a precursor to humins or undergo further esterification reactions.

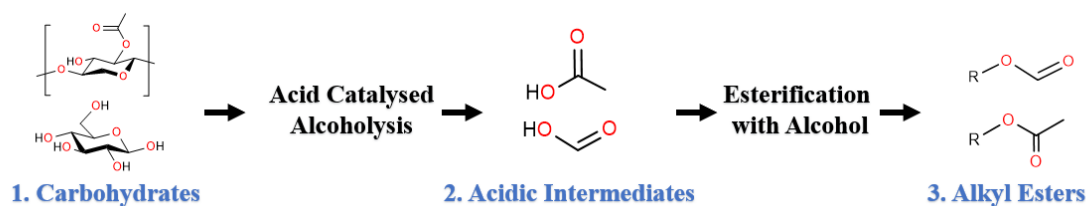


Figure 11. Schematic representation of the acid-catalysed alcoholysis of carbohydrates. Lignocellulosic polysaccharides are first depolymerised to acidic intermediates such as levulinic and formic acids, which subsequently undergo esterification with alcohol to form alkyl esters including alkyl levulinates and alkyl formates.

Despite the clear mechanistic basis for their formation, co-products beyond levulinates remain largely neglected in the alcoholysis literature. While some studies have reported ether yields, the systematic quantification of alkyl formates, acetates, and furfural is almost entirely absent. As a result, current understanding of the secondary product spectrum is

incomplete, and the true carbon efficiency of alcoholysis remains obscured. This thesis directly addresses this critical gap by providing to our knowledge, the first systematic identification and quantification of *n*-butyl formate, *n*-butyl acetate, and furfural, delivering novel insights into the co-product distribution and advancing the fundamental understanding of alcoholysis chemistry.

2.2.4 Humin Formation

Humins are insoluble, carbonaceous polymeric by-products formed predominantly through the acid-catalysed dehydration and condensation of intermediates such as hydroxymethylfurfural and furfural, alongside contributions from phenolic fragments in lignin-rich fractions [128]. Their formation reduces levulinate yields and can complicate reactor operation due to fouling and solid accumulation. However, recent work has shifted the perception of humins from unavoidable waste streams to potentially valuable co-products. Their carbon-rich, aromatic, and thermally stable nature aligns them with applications similar to biochar, including use as soil amendments, long-term carbon sequestration agents, and replacements for peat in horticultural substrates [129-131]. Studies have demonstrated their potential in heavy metal remediation through soil stabilisation [129], in green remediation strategies for contaminated soils [130], and even as redox-active materials when sulphur is incorporated during acid-catalysed formation [132]. More advanced valorisation pathways are under development, where humins serve as precursors for functional carbons, foams, or resins, contributing positively to the sustainability profile of lignocellulosic biorefineries [131].

In experimental alcoholysis studies, humins are typically quantified gravimetrically after centrifugation and drying, but their composition and yields vary widely with feedstock and reaction conditions [44, 128]. This thesis advances the field by providing systematic quantification and characterisation of humins, including ultimate analysis and detailed reporting of carbon yields. While the precise molecular mechanisms of humin formation remain complex and are beyond the scope of this work, the results presented here establish a robust foundation for understanding their occurrence and impact in alcoholysis systems.

2.2.5 Mechanistic Insights and Solvent Effects

Recent mechanistic studies have advanced understanding of alcoholysis by clarifying the role of solvent effects. Density functional theory (DFT) calculations have demonstrated that explicit inclusion of solvent molecules reduces the energy barriers of key steps, especially proton transfer, glycosidic bond cleavage, and nucleophilic substitution [52, 57, 133]. In ethanolysis, ethanol-assisted proton shuttling accelerates glucose–fructose isomerisation and stabilises ethyl glucoside intermediates, thereby enhancing ethyl levulinate formation [52]. Butanol, with its lower polarity and larger molecular size, alters solvent–solute interactions and leads to different balances of levulinate, ether, and ester products.

Taken together, these findings underscore the complexity of alcoholysis chemistry. Alkyl levulinate formation competes with solvent-consuming etherification and esterification pathways, while humins and soluble unknowns represent unavoidable carbon sinks. Advances in mechanistic modelling now provide a framework for disentangling these competing pathways, but consistent experimental reporting of all major and minor products remains critical for further progress.

2.3 Ethanolysis

2.3.1 Carbohydrate Substrates

The conversion of model carbohydrates to ethyl levulinate under ethanolysis conditions has been extensively studied, providing insight into relative reactivity trends and mechanistic pathways. Among monomeric sugars, fructose consistently affords the highest ethyl levulinate yields, often exceeding 70 mol% under Brønsted acid catalysis, whereas glucose typically gives lower yields in the range of 40–50 mol% with similar catalysts, though improvements up to 81 mol% have been reported when Lewis acid co-catalysts are employed [61, 68, 69, 87]. The disaccharide sucrose yields intermediate values, reflecting the need for hydrolytic cleavage before monomer conversion [58, 68, 70, 74, 77, 81, 83, 86, 92, 94, 98]. At the polymeric level, inulin, a polyfructan, gives markedly higher yields than cellulose, its polyglucan counterpart, reinforcing the intrinsic reactivity advantage of fructose-derived units [61, 66, 89]. By contrast, cellulose ethanolysis typically affords moderate yields of 40–55 mol%, with a maximum of 75 mol% achieved using combined Lewis–Brønsted systems

[100, 104, 105, 134]. These comparative observations establish a general reactivity order of fructose > inulin > sucrose > glucose > cellulose > raw biomass [66].

The superior performance of fructose is often rationalised in terms of the canonical ethanolysis pathway, which proceeds via dehydration to 5-hydroxymethylfurfural, followed by ethanol-mediated etherification to 5-ethoxymethylfurfural, and subsequent rehydration to ethyl levulinate [61]. In this context, fructose undergoes dehydration to 5-hydroxymethylfurfural far more readily than glucose due to its furanose-rich structure, which provides a lower-energy transition state for enolisation and subsequent water elimination [52, 61]. Glucose, in contrast, requires acid-catalysed isomerisation to fructose before efficient 5-hydroxymethylfurfural formation can occur, imposing an additional kinetic barrier [61, 87, 133].

However, recent experimental evidence, including the conditions studied in this work, indicates that an alternative route via alkyl glucosides can predominate. In this pathway, glucose first reacts with ethanol to form ethyl glucosides, which subsequently convert to ethyl levulinate without requiring prior dehydration to 5-hydroxymethylfurfural. This helps to explain why glucose and cellulose often benefit from the presence of Lewis acids (e.g., SnO_2 , $\text{Y}(\text{OTf})_3$), which not only catalyse glucose isomerisation but may also influence the relative flux through glucoside- versus 5-hydroxymethylfurfural-derived intermediates [87, 100].

Sucrose represents an intermediate case: it must first undergo hydrolysis to glucose and fructose, after which the balance between glucoside formation and 5-hydroxymethylfurfural dehydration dictates the yield. This dependence on hydrolytic cleavage explains why sucrose typically gives lower yields than pure fructose but higher than glucose under identical conditions [58, 68, 77, 81]. Similarly, the markedly lower yields observed with cellulose stem from both the recalcitrance of the polymeric matrix and the slower kinetics of glucose-to-fructose isomerisation [104, 134]. The comparison with inulin highlights that polymer depolymerisation is not the rate-determining step in ethanolysis, since fructose units are readily liberated and converted, but rather that the monomer identity and operative mechanistic pathway govern ethyl levulinate formation efficiency [66].

Overall, the observed substrate-dependent yield trends are consistent with competing mechanistic routes. While fructose retains a persistent reactivity advantage through facile 5-

hydroxymethylfurfural formation, under many conditions the alkyl glucoside pathway can represent the dominant contributor to ethyl levulinate production. This dual mechanistic framework provides a rationale for catalyst design incorporating Lewis acid sites to promote glucose isomerisation and glucoside conversion and underpins strategies to improve the ethanolysis of cellulose and biomass-derived feedstocks.

2.3.2 Lignocellulosic Biomass Substrates in Ethanolysis

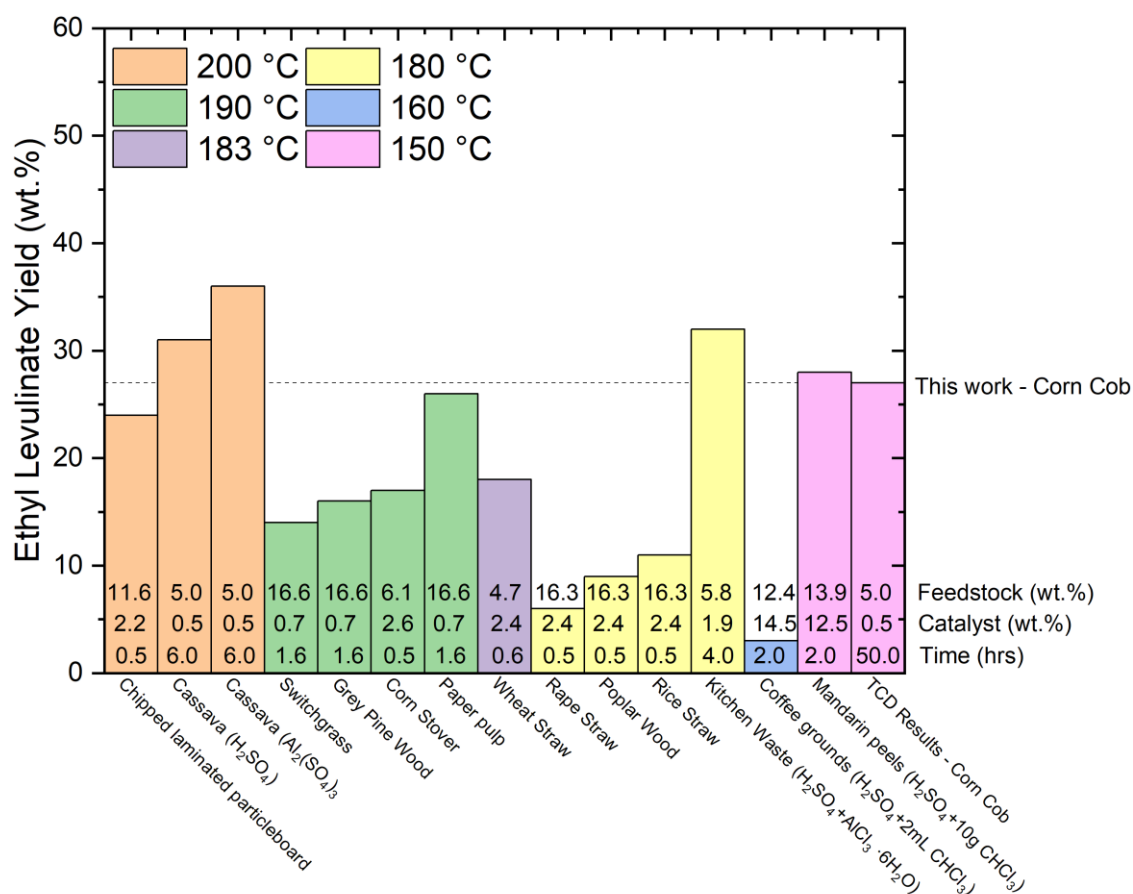


Figure 12. Literature review of experimental yields of ethyl levulinate categorized by temperature from various real biomasses [106, 107, 111, 113, 115-117, 135, 136]. The feedstock loading (wt.%), catalyst loading (wt.%), and reaction times are displayed at the bottom of each column. All reactions are a one-pot process and use sulphuric acid as the catalyst unless otherwise stated.

Ethanolysis has also been applied directly to lignocellulosic biomass, with studies reporting the conversion of corn cob, wheat straw, cassava, bamboo, citrus peel, and other agricultural residues, as well as forestry by-products and algal biomass [106, 108, 110, 113, 115-118]. The wide diversity of tested substrates highlights the broad applicability of one-pot alcoholysis systems for valorising designated wastes. Reported ethyl levulinate yields vary substantially between feedstocks, with higher values generally associated with

cellulosic-rich residues such as bamboo and corn cob, and lower values observed for lignin-rich or unconventional feedstocks such as algae. These studies demonstrate the feasibility of producing liquid fuel precursors directly from raw biomass in a single step, although current yields remain lower than those observed for model carbohydrates.

A persistent limitation in this literature is the lack of standardisation in yield reporting. Many reports use mass yields (wt%), calculated relative to the starting biomass, while others report molar yields normalised only to the cellulose fraction [110, 113, 116]. This limitation is addressed in Section 2.6, where a rigorous yield framework is developed.

The spread of yields reported for different biomasses under one-pot ethanolysis is illustrated in Figure 12. Reported ethyl levulinate yields span from below 3 wt% to above 50 wt% depending on the feedstock, temperature, and operating conditions [106, 107, 111, 113, 115-117, 135, 136]. In general, yields from real biomass substrates are significantly lower than those from model carbohydrates, with the higher values observed for corn cob (27%, this thesis), mandarin peel (28%) [115], and cassava (31–36%) [113, 118]. Given that ethyl levulinate formation arises predominantly from the cellulosic fraction, these values are consistent with the polysaccharide composition of the respective feedstocks. Notably, nine of the thirteen studies surveyed report ethyl levulinate yields below 25%, reflecting both the recalcitrance of lignocellulosic materials and the variability in biomass composition.

Despite these limitations, one-pot ethanolysis of lignocellulosic biomass remains a comparatively underexplored but highly promising valorisation pathway. Compared with multi-step hydrolysis or pyrolysis approaches, the direct production of liquid intermediates in ethanol offers simplicity, waste minimisation, and compatibility with existing fuel blending practices. Its capacity to utilise low-value residues such as corn cob, wheat straw, and other designated wastes positions it as a viable strategy for decarbonising road transport, aligning with both circular economy principles and advanced biofuel deployment targets.

2.3.3 Catalysis in Ethanolysis

The majority of studies on ethanolysis have focused on the influence of the catalyst on the resulting yield of ethyl levulinate. Both homogeneous and heterogeneous Brønsted and

Lewis acids, as well as combinations of the two, have been investigated extensively [52, 58, 68-70, 72-75, 78-88, 125, 133, 137, 138].

Homogeneous catalysts: The archetypal catalyst for ethanolysis is sulphuric acid (H_2SO_4), one of the most widely produced industrial chemicals, manufactured almost exclusively via the contact process, in which sulphur or sulphur containing feedstocks are oxidised to sulphur dioxide, catalytically converted to sulphur trioxide, and subsequently absorbed to form concentrated H_2SO_4 [139]. The scale and maturity of this production route underpin the low cost and widespread availability of sulphuric acid at industrial scale. However, its manufacture is associated with non negligible embodied energy and greenhouse gas emissions, arising primarily from sulphur oxidation, gas compression, and thermal management within the process. As a result, while H_2SO_4 is routinely employed as a benchmark homogeneous catalyst in ethanolysis studies, consideration of acid loading and catalyst efficiency remains relevant from both economic and sustainability perspectives.

Using H_2SO_4 , moderate yields of ethyl levulinate have been obtained from a variety of substrates, including 72 mol% from fructose [68], 45 mol% from glucose [69], 51 mol% from cellulose [134], and 51 wt% from cellulosic pulp derived from bamboo [108]. Lewis acids have been introduced to improve performance by catalysing glucose isomerisation to fructose, thereby enabling higher ethyl levulinate yields. For example, the combination of SnO_2 with zeolite H-USY afforded 81 mol% yield from glucose [87], while $\text{Y}(\text{OTf})_3$ with H_3PO_4 achieved 75 mol% from cellulose [100]. These examples demonstrate that synergistic Lewis–Brønsted systems can elevate the maximum ethyl levulinate yields from glucose and cellulose to levels approaching those from fructose. Nevertheless, when considered broadly, more exotic Brønsted or Lewis acids generally offer little improvement over H_2SO_4 alone, as reaction rate and yield are ultimately determined by proton concentration, regardless of its source.

Heterogeneous catalysts: A wide variety of solid catalysts have been studied, including zeolites [59, 69, 73, 79, 81, 82, 85, 97, 140], sulfonated nanomaterials [70, 72, 75, 83, 95, 98, 141], and polyoxometalates [74, 76, 83, 85, 88, 92, 101, 103, 142]. Heterogeneous systems are often justified in terms of potential process intensification, offering simplified catalyst separation and recycling. However, while this is feasible for model substrates such as glucose, fructose, and cellulose, practical difficulties arise with raw biomass. Ethanolysis of lignocellulosic feedstocks generates insoluble carbonaceous solids known as humins,

Chapter 2. Literature Review of Alcoholysis

which deposit on catalyst surfaces and prevent efficient recovery and reuse [44]. As a result, the benefits of heterogeneous catalysis are often negated under realistic process conditions. For this reason, H_2SO_4 is the most widely employed catalyst in the literature and is also the benchmark used in this work. Importantly, techno-economic assessments have confirmed that sulphuric acid remains the only catalyst capable of rendering ethyl levulinate production commercially viable at scale, due to its unique balance of low cost, availability, and catalytic strength [37].

Table 1. Reported catalytic systems for the ethanolysis of glucose to ethyl levulinate.

Ethanolysis of Glucose						
Catalyst	Feedstock loading (g)	Catalyst loading (g)	Ethanol loading (g)	Temp. (°C)	Time (hrs)	EL yield (mol%)
Inorganic mineral acids and metal salts						
H_2SO_4	1.0	0.0	39.4	180	0.5	45
H_2SO_4	1.0	0.0	26.5	200	6.0	34
H_2SO_4	1.0	0.0	39.2	200	1.5	37
H_2SO_4	1.0	0.0	39.5	210	0.5	45
HReO_4	1.0	0.1	21.7	160	16.0	27
$\text{Fe}_2(\text{SO}_4)_3$	1.0	2.2	9.00	170	2.0	39
$\text{La}_2(\text{SO}_4)_3$	1.0	2.2	9.00	170	2.0	29
$\text{Ce}(\text{SO}_4)_2$	1.0	2.2	9.00	170	2.0	29
Sulfonic acids, sulfonate salts, and their combination						
HDS-3.6	1.0	0.4	390	170	8.0	25
5-Cl-SHPAO	1.0	0.3	20.0	160	8.0	61
AC-Fe-SO ₃ H	1.0	0.5	52.7	200	3.0	19
Sulphonated char	1.0	0.2	26.5	200	6.0	37
Polyoxometalate (POM)-based catalysts						
$\text{KH}_2\text{PW}_{12}\text{O}_{40}$	1.0	0.8	35.5	150	2.0	15
$\text{Ti}_{0.75}\text{PW}_{12}\text{O}_{40}$	1.0	0.4	17.5	120	6.0	21
$[\text{TMEDAPS}]_3 [\text{PW}_{12}\text{O}_{40}]_2$	1.0	1.0	64.0	150	24.0	20
DPW-CeSiM	1.0	0.8	15.8	170	4.0	56
Zeolite-based catalysts						
HY	1.0	1.0	64.0	170	12.0	39
H-B	1.0	0.6	31.6	160	20.0	28
H-USY	1.0	0.6	31.6	160	20.0	41
USY	1.0	0.2	7.90	200	0.2	15
USY	1.0	0.0	39.4	180	2.0	47
USY + H_2SO_4	1.0	0.0	39.4	180	2.0	51
$\text{Sn-}\beta + \text{ZrH}_2\text{PW}_{12}\text{O}_{40}$	1.0	0.5	26.4	180	3.0	54
$\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{H-ZSM-5}$	1.0	1.5	39.2	160	2.0	19
H-USY + SnO_2	1.0	0.5	15.8	180	3.0	81
Metal oxides and tungsten disulfide catalysts						
$\text{SO}_4^{2-}/\text{ZrO}_2$	1.0	0.0	15.8	200	3.0	29
$\text{SO}_4^{2-}/\text{ZrO}_2/\text{Al}_2\text{O}_3$	1.0	0.5	61.1	200	5.0	37
Grafted $\text{SO}_4^{2-}/\text{ZrO}_2/\text{SBA-}$	1.0	0.5	25.6	140	24.0	31
$\text{SO}_4^{2-}/\text{ZrO}_2\text{PMO-SO}_3\text{H}$	1.0	1.0	64.0	170	12.0	42
$\text{SO}_3\text{H-Al/Silica}$	1.0	0.3	26.3	180	12.0	48
This thesis - H_2SO_4						
H_2SO_4	1.0	0.05	19.0	150	100	67

Reported catalytic systems for the ethanolysis of glucose to ethyl levulinate [52, 58, 68-70, 72-75, 78-88, 125, 133, 137, 138], grouped by catalyst class. All experiments use glucose as the feedstock with loadings normalised to 1.0 g, and catalyst and ethanol amounts scaled accordingly. Reaction conditions are based on conventional heating. Ethyl levulinate yields are expressed as molar percentages. Literature data are compared with results generated in this work (this thesis – H_2SO_4).

Performance versus practicality: To provide a fair comparison across different catalyst classes, the dataset shown in Figure 13 and Table 1 is restricted to glucose as the feedstock, which represents the most extensively studied carbohydrate and therefore provides the largest and most internally consistent dataset. When viewed in this way, no single catalyst class can be identified as universally superior in achieving higher steady-state yields. As shown in Figure 13, four of the five generic catalyst classes achieve comparably high ethyl levulinate yields (56–81 mol%) from glucose, with outcomes strongly dependent on reaction time, temperature, and catalyst loading [52, 58, 68-70, 72-75, 78-88, 125, 133, 137, 138]. Zeolites have occasionally been reported to give marginally higher yields, though the evidence is inconclusive. Importantly, variability in reported performance often reflects differences in experimental design rather than intrinsic catalytic activity. Attempts at statistical treatment of the glucose dataset, such as multiple linear regression or principal component analysis, have not yielded robust models due to the broad heterogeneity of reported conditions and insufficient data density but are reported in the appendix of this thesis.

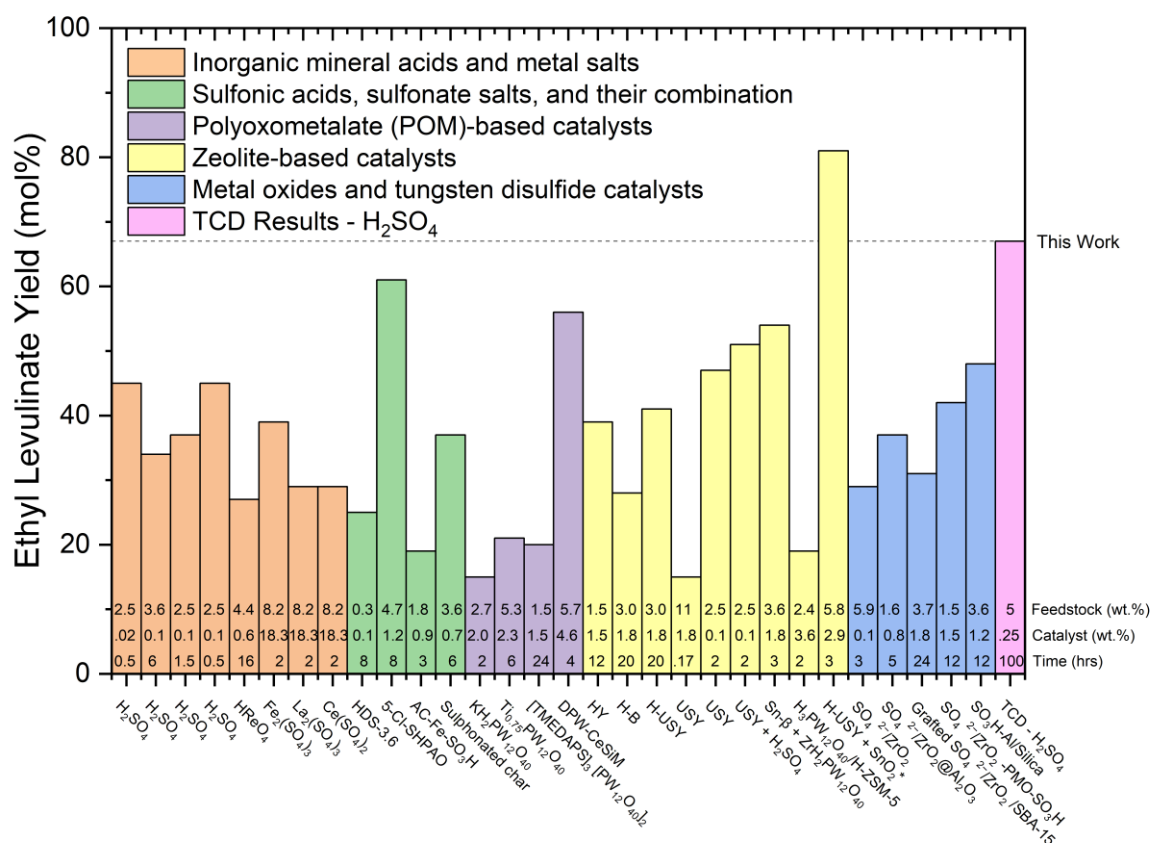


Figure 13. Literature review of experimental yields of ethyl levulinate from glucose using various catalyst types [52, 58, 68-70, 72-75, 78-88, 125, 133, 137, 138]. All reaction systems use conventional heating and a one-pot process. The glucose loading (wt.%), catalyst loading (wt.%), and reaction times (hrs) are displayed at the bottom of each column.

Overall Figure 13 highlights the absence of a coherent trend across catalyst classes and reinforces the conclusion that while heterogeneous catalysts may appear attractive in controlled model systems, issues of fouling, recyclability, and cost limit their practical deployment. Techno-economic analysis strengthens this view, showing that despite decades of catalyst development, only sulphuric acid offers the cost-effectiveness and scalability required to make ethyl levulinate production commercially viable [37].

2.3.4 Ether Formation in Ethanolysis

Dialkyl ethers are an unavoidable co-product of alcoholysis reactions, arising from the acid-catalysed dehydration of two alcohol molecules, with the concomitant formation of one molecule of water (Figure 7). In ethanolysis, this side reaction leads to the formation of diethyl ether, and because alcohol is generally present in large excess relative to the carbohydrate substrate, diethyl ether yields can be substantial [35]. For example, Mascal et al. reported that 67 mol% of ethanol was converted to diethyl ether during the ethanolysis of dried conifer wood with 2-naphthalenesulfonic acid at 200 °C for 4 hours [46]. Zhu et al. subsequently demonstrated that employing lower acid concentrations significantly reduces diethyl ether formation, though at the expense of slower rates of ethyl levulinate production [47].

The relative rates of diethyl ether and ethyl levulinate formation are therefore of enormous importance for process performance. On the one hand, diethyl ether represents a valuable industrial chemical and fuel additive in its own right; on the other, uncontrolled ether formation consumes ethanol and reduces the net carbon efficiency of the ethanolysis process. Despite this, most experimental studies of biomass ethanolysis have either neglected to quantify diethyl ether formation or have not reported its time-resolved evolution. Without such data, it is not possible to accurately evaluate the overall efficiency or techno-economic viability of the process.

In this context, the subsequent ethanolysis study (Chapter 5) addresses these shortcomings by systematically examining the relationship between ethyl levulinate yield and diethyl ether formation across three representative systems:

1. Glucose + H₂SO₄ + Ethanol (i.e., the ideal case)

2. Cellulose + H₂SO₄ + Ethanol (i.e., the intermediate case)
3. Corn cob + H₂SO₄ + Ethanol (i.e., the realistic case)

By capturing the interplay between ethyl levulinate and diethyl ether formation as a function of reaction time, acid concentration, and feedstock loading, this work provides a complete and internally consistent dataset that enables a more accurate assessment of the techno-economic viability of ethanolysis for the production of advanced biofuels.

2.4 Butanolysis

Compared to ethanolysis, the one-pot butanolysis of carbohydrates and biomass has received significantly less attention. Nonetheless, butyl levulinate is an especially attractive target molecule, as butyl esters display superior combustion and blending properties relative to ethyl esters, making them highly promising advanced biofuels for road transport [40]. The available literature is therefore limited but strategically important, highlighting the need for systematic studies to establish reliable yield trends, catalytic performance, and process viability.

2.4.1 Carbohydrate Substrates in Butanolysis

The yield trends reported for butanolysis generally mirror those observed in ethanolysis, though the available literature is far more limited. As shown in Figure 14 and Table 2, fructose consistently affords the highest yields of *n*-butyl levulinate, with values above 65 wt% under homogeneous acid catalysis [143, 144]. Glucose yields are lower, typically in the 35–55 wt% range [145, 146]. Cellulose yields are highly variable (30–55 wt%), depending on catalyst type and process configuration, with studies reporting *n*-butyl levulinate production using ionic liquids [147], metal sulphates [148], and sulphuric acid [36]. This thesis demonstrates that xylan affords moderate *n*-butyl levulinate yields, consistent with the more complex mechanistic requirements of hemicellulose conversion. This insight establishes unequivocally that hemicellulose is a significant contributor to *n*-butyl levulinate formation, overturning the long-standing assumption that only cellulose drives alkyl levulinate yields.

The overall order of substrate reactivity for levulinate yields is therefore established as fructose > glucose > cellulose > biomass > xylan, consistent with ethanolysis, but without the benefit of systematic comparative studies. While the scattered reports establish that *n*-butyl levulinate can be obtained from a range of carbohydrate substrates under one-pot conditions, the absence of a consistent and systematic dataset represents a major gap in the literature. This work addresses that gap by benchmarking carbohydrate-derived *n*-butyl levulinate yields under controlled conditions, thereby providing the basis for fair substrate comparisons of butanolysis.

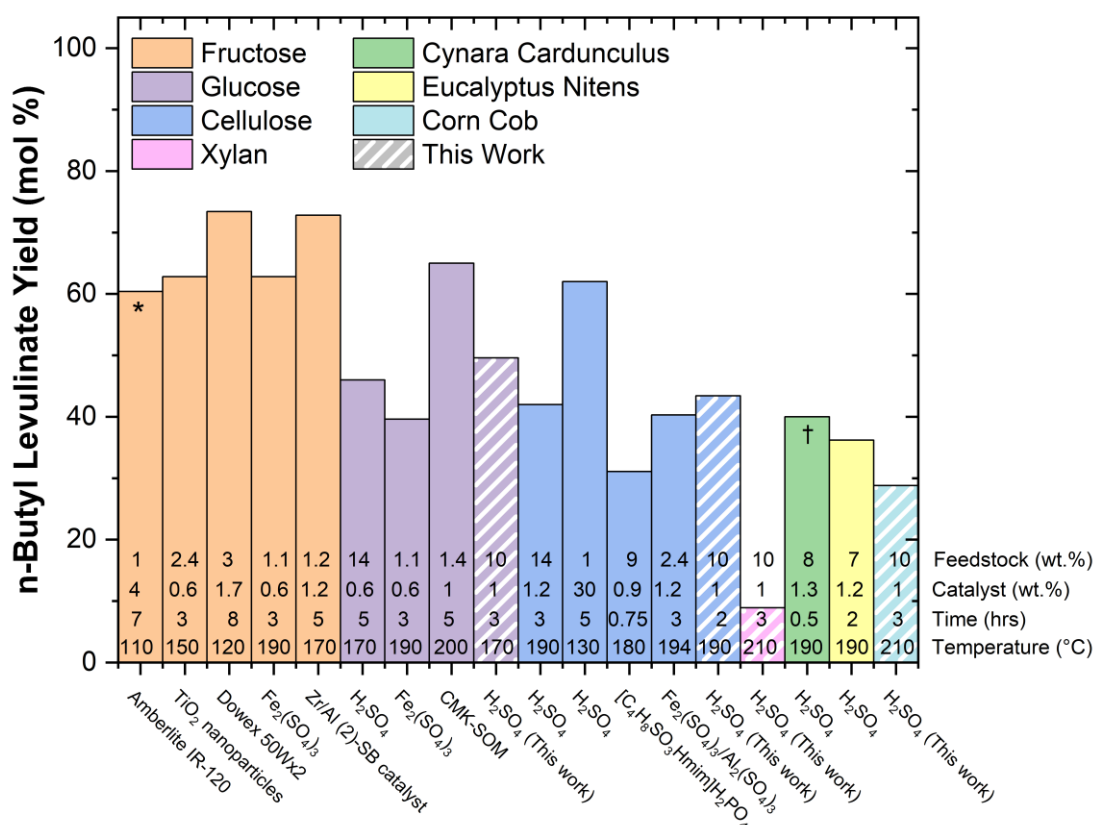


Figure 14. Molar yields of *n*-butyl levulinate obtained from various feedstocks [36, 120, 121, 143-151]. Yields are expressed according to the novel molar method described by Equation 13. Each data point represents a one-pot system containing only butanol, catalyst, and feedstock, with the striped columns indicating this work. The asterisk (*) indicates the use of a co-solvent system comprising γ -valerolactone (GVL) and butanol (30/70 wt%) and (†) indicates that microwave-assisted heating and steam explosion pretreatment were employed.

2.4.2 Lignocellulosic Biomass Substrates in Butanolysis

Reports on butanolysis of real biomass substrates are sparse. Published examples include *Cynara cardunculus* and *Eucalyptus nitens*, which afford modest *n*-butyl levulinate yields under acid catalysis [120, 121]. The lack of systematic investigation across different

feedstocks, catalysts, and conditions has so far prevented the establishment of reliable benchmarks for biomass butanolysis.

A persistent problem in this literature is the conventional method of yield reporting, which almost exclusively normalises to the cellulose fraction of the biomass. This practice overlooks contributions from hemicellulose, leading to systematic overestimation of molar yields and misrepresentation of overall molecular efficiency [35]. In a novel finding, this work demonstrates that xylan, and thus hemicellulose fractions, also contribute to *n*-butyl levulinate formation under one-pot conditions. This challenges prior assumptions and underscores the need to move beyond conventional yield metrics.

Accordingly, this thesis introduces a novel yield reporting framework (see Section 2.6), applied here to corn cob as a benchmark case. This approach provides the first realistic assessment of molar efficiency in biomass butanolysis and establishes a foundation for fair techno-economic evaluation.

2.4.3 Catalysis in Butanolysis

As with ethanolysis, most studies of butanolysis have centred on the influence of the catalyst on *n*-butyl levulinate yield. Both homogeneous and heterogeneous Brønsted and Lewis acids have been investigated, though the dataset remains far smaller than for ethanolysis.

Homogeneous catalysts: Sulphuric acid (H_2SO_4) is the archetypal catalyst for butanolysis, widely employed due to its low cost, industrial availability, and high catalytic efficiency [151]. Although corrosive and difficult to recycle, H_2SO_4 provides consistently high *n*-butyl levulinate yields from both model sugars and lignocellulosic feedstocks, making it the pragmatic choice for biomass processing. Other homogeneous systems, such as $\text{Fe}_2(\text{SO}_4)_3$ [80] and $\text{Al}_2(\text{SO}_4)_3$ [105, 145], have been shown to catalyse glucose and cellulose butanolysis with moderate efficiency. These studies confirm that Lewis and Brønsted acid combinations can enhance yields, but none have surpassed the consistency or scalability of H_2SO_4 .

Heterogeneous catalysts: A variety of solid catalysts have also been investigated, including TiO_2 nanoparticles [149], ion-exchange resins [144], sulfonated mesoporous

Chapter 2. Literature Review of Alcoholysis

carbons [146], acidic ionic liquids [147], and zeolitic or oxide-based systems [150]. These catalysts are often promoted as greener alternatives, offering the potential for separation and reuse. However, as in ethanolysis, biomass butanolysis produces insoluble carbonaceous residues (humins) that deposit on catalyst surfaces, inhibiting recyclability and rapidly diminishing activity [151]. Furthermore, heterogeneous systems generally require higher catalyst loadings than H_2SO_4 , increasing costs and limiting scalability.

Table 2. Literature summary of one-pot butanolysis: feedstocks, catalysts, operating conditions, and butyl levulinate (BL) yields [36, 120, 121, 143-151].

One-Pot Butanolysis Literature review summary							
Feedstock	Catalyst	Feedstock (wt.%)	Catalyst (wt.%)	Temp. (°C)	Time (hrs)	BL yield (mol%)	BL yield (wt.%)
Fructose*	Amberlite IR-120	1	4	110	7	60.4	57.7
Fructose	TiO_2 nanoparticles	2.4	0.6	150	3	62.8	60.0
Fructose	Dowex 50Wx2	3	1.7	120	8	73.4	70.2
Fructose	$\text{Fe}_2(\text{SO}_4)_3$	1.1	0.6	190	3	62.8	60.0
Fructose	Zr/Al (2)-SB catalyst	1.2	1.2	170	5	72.8	69.6
Glucose	H_2SO_4	14	0.6	170	5	46.0	44.0
Glucose	$\text{Fe}_2(\text{SO}_4)_3$	1.1	0.6	190	3	39.6	37.9
Glucose	CMK-SOM	1.4	1	200	5	65.0	62.1
Glucose (this work)	H_2SO_4	10	1	170	3	49.6	47.6
Cellulose	H_2SO_4	14	1.2	190	3	42.0	44.6
Cellulose	$[\text{C}_4\text{H}_8\text{SO}_3\text{Hmim}]\text{H}_2\text{PO}_4$	9	0.9	180	0.75	31.1	33.0
Cellulose	H_2SO_4	1	30	130	5	62.0	65.9
Cellulose	$\text{Fe}_2(\text{SO}_4)_3/\text{Al}_2(\text{SO}_4)_3$	2.4	1.2	194	3	40.3	42.8
Cellulose (this work)	H_2SO_4	10	1	190	2	43.4	46.2
Xylan (this work)	H_2SO_4	10	1	210	3	8.90	9.70
Cynara cardunculus	H_2SO_4	8	1.3	190	0.5	40.0	26.4
Eucalyptus nitens	H_2SO_4	7	1.2	190	2	36.2	16.2
Corn Cob (this work)	H_2SO_4	10	1	210	3	28.8	17.5

Performance versus practicality. Across the literature, *n*-butyl levulinate yields above 60 wt% with isolated sugars as feedstocks have been achieved using both homogeneous and heterogeneous catalysts, but the lack of standardised conditions makes comparisons unreliable. In contrast to ethanolysis, where larger datasets have allowed limited statistical analysis, the butanolysis literature remains too sparse and fragmented for such approaches. However, the results of this work demonstrate that butanolysis behaves in a manner consistent with ethanolysis under equivalent reaction conditions. As shown by comparing Figure 12 and Figure 13 (ethanolysis) with the butanolysis data presented in Figure 14 and

Table 2, the relative performance of catalyst classes follows the same trend: H_2SO_4 provides the most robust and reproducible yields, Lewis–Brønsted acid combinations enhance conversion of glucose via isomerisation, and heterogeneous systems are constrained by humin fouling and recyclability issues. This suggests that catalyst behaviour can be assumed to translate between ethanolysis and butanolysis, with differences arising primarily from the solvent environment rather than mechanistic divergence.

Importantly, techno-economic assessments reinforce this conclusion: despite ongoing research into alternative systems, sulphuric acid remains the only catalyst capable of rendering alkyl levulinate production commercially viable at scale [35, 37, 151].

2.5 Kinetic Modelling of Alcoholysis

Kinetic modelling of alcoholysis remains underdeveloped, with only a handful of studies available for ethanolysis and none for butanolysis. Table 3 summarises the limited kinetic models reported for ethanolysis of fructose and glucose under homogeneous acid catalysis. Flannelly et al. [61] developed a mass-conserved model that enforced conservation of fructose flux, enabling quantitative testing of mechanistic routes through hydroxymethylfurfural (HMF), ethoxymethyl furfural (EMF), and ethyl glucosides. Howard [51] subsequently advanced this approach to a fully element-conserved framework, incorporating thermodynamic reversibility and computational chemistry consistency, thereby providing the most rigorous ethanolysis model prior to this thesis. Zhu et al. [47] resented simplified schemes for glucose conversion to ethyl levulinate and acetate, incorporating humin and unidentified soluble products with high statistical fidelity ($R^2 \approx 0.99$) but without comprehensive mechanistic closure. Overall, while these contributions have advanced understanding, they remain restricted to ethanolysis of simple sugars, emphasise different mechanistic assumptions (fructose–HMF–EMF versus glucoside pathways), and have not yet been extended to butanolysis or lignocellulosic feedstocks. This scarcity underscores the immaturity of the field and motivates the use of surrogate modelling in this thesis to provide a mass-balanced, scalable framework for capturing product distributions based solely on the biochemical composition of the feedstock.

Chapter 2. Literature Review of Alcoholysis

Table 3. Literature review of the kinetic modelling of the ethanolysis of carbohydrates using a sulphuric acid catalyst for a closed homogeneous isothermal reaction system.

Literature Review of Ethanolysis Kinetic Models					
Feedstock	Reaction Time (mins)	Reaction Temp. (°C)	Reaction mechanism	Fidelity	Ref.
Fructose	480	78	$Fructose \xrightarrow{H^+} HMF + 3H_2O$	$R^2 = 0.75$	[61]
			$HMF + Ethanol \xrightarrow{H^+} EMF + H_2O$		
			$EMF + 2H_2O \xrightarrow{H^+} HMF + Formic\ acid$		
			$Fructose + Ethanol \xrightarrow{H^+} Ethyl\ glucosides + H_2O$		
			$Ethyl\ glucosides + H_2O \xrightarrow{H^+} fructose + Ethanol$		
Fructose	250	180	$Fructose \xrightarrow{H^+} HMF + 3H_2O$	$R^2 = 0.93$	[51]
			$HMF + Ethanol \xrightarrow{H^+} EMF + H_2O$		
			$EMF + 2H_2O \xrightarrow{H^+} HMF + Formic\ acid$		
			$Fructose + Ethanol \xrightarrow{H^+} Ethyl\ glucosides + H_2O$		
			$Ethyl\ glucosides + H_2O \xrightarrow{H^+} fructose + Ethanol$		
Glucose	1600	180	$Fructose \xrightarrow{H^+} Unknowns$	$R^2 = 0.90$	[51]
			$Glucose + Ethanol \xrightarrow{H^+} Ethyl\ glucosides + H_2O$		
			$Ethyl\ glucosides + H_2O \xrightarrow{H^+} Glucose + Ethanol$		
			$Ethyl\ glucosides \xrightarrow{H^+} Ethyl\ levulinate + Formic\ acid + H_2O$		
			$Glucose \xrightarrow{H^+} Unknowns\ A$		
Glucose	210	160	$Ethyl\ glucosides \xrightarrow{H^+} Unknowns\ B$	$R^2 = 0.986$	[47]
			$Glucose \xrightarrow{H^+} Ethyl\ levulinate + Ethyl\ acetate$		
Glucose	210	180	$Glucose \xrightarrow{H^+} Humin + unidentified\ soluble\ products$	$R^2 = 0.986$	[47]
			$Glucose \xrightarrow{H^+} Ethyl\ levulinate + Ethyl\ acetate$		
Glucose	210	200	$Glucose \xrightarrow{H^+} Ethyl\ levulinate + Ethyl\ acetate$	$R^2 = 0.986$	[47]

2.6 Yield Representations for Biomass Conversion

2.6.1 Importance of Yield Metrics

Yield is the most widely reported performance indicator in biomass conversion studies, yet the way it is defined and calculated varies considerably between different technologies, feedstocks, and target products. This variation has major implications, not only for scientific communication but also for the comparability of results across studies, reactor designs, and scales. For example, while thermochemical routes such as pyrolysis and gasification often

report yields in terms of mass fractions or energy yields, biochemical systems rely more heavily on molar yields to describe substrate-to-product stoichiometry [67, 152]. In catalytic chemical conversions, particularly alcoholysis, the choice of yield metric directly influences perceived molecular efficiency and process selectivity, with conventional approaches often overestimating yields when only the cellulose fraction of biomass is considered [120, 121].

The importance of consistent yield representation extends beyond academic reporting. In techno-economic assessment and life-cycle analysis yield metrics underpin calculations of process efficiency, carbon conversion, and sustainability. Inaccuracies or inconsistencies in yield reporting can therefore distort economic modelling, obscure environmental impacts, and hinder scale-up decisions [153, 154]. While energy-based yields are valuable in mature technologies such as gasification or combustion, in catalytic liquid-phase processes such as alcoholysis more appropriate measures include mass yield, molar yield, carbon yield, and volumetric productivity metrics such as space-time yield. A multi-metric approach that combines these perspectives is increasingly recognised as essential for robust evaluation of emerging biomass conversion technologies [155, 156].

2.6.2 Common Yield Metrics Across Biomass Conversion Technologies

Different biomass conversion pathways employ distinct yield metrics depending on the chemistry, feedstock complexity, and product distribution of the process. No single representation is sufficient to describe performance across all systems, so a range of approaches has developed in the literature. Representative equations are provided below for reference.

2.6.2.1 Mass yield (%)

$$Yield\ (wt.\ \%) = \frac{Product\ (g)}{Feedstock\ (g)} \times 100 \quad (4)$$

Mass yield expresses the recovered mass of a target product relative to the dry mass of the input feedstock. It is commonly used in thermochemical processes such as pyrolysis and hydrothermal liquefaction, as well as in biodiesel transesterification [67, 157]. Although

simple and widely applicable, mass yield does not capture the molecular efficiency of catalytic reactions or provide insight into competing pathways.

2.6.2.2 Molar yield (%)

$$Yield (mol\%) = \frac{Product (mol)}{Feedstock (mol)} \times 100 \quad (5)$$

Molar yield measures the moles of product formed relative to the moles of substrate consumed. This metric is especially valuable in biochemical conversions such as fermentation, where it reflects the stoichiometric efficiency of microbial metabolism [152]. In catalytic chemical conversions including alcoholysis, molar yield indicates pathway efficiency and selectivity but can be misleading when applied to real biomass, as overestimation occurs if only moles of cellulose is considered [116, 120, 121].

2.6.2.3 Carbon yield (%)

$$Carbon\ yield\ (mol\%) = \frac{Moles\ of\ C\ formed\ as\ product}{Moles\ of\ C\ in\ feedstock} \times 100 \quad (6)$$

Carbon yield accounts for the fraction of carbon atoms from the feedstock incorporated into the desired product. This is particularly relevant in life-cycle assessment and carbon accounting, as it provides transparency on carbon allocation between products, by-products, and losses [158, 159]. For alcoholysis, this approach is especially important because only a fraction of the carbon in alkyl levulinates originates from the carbohydrate fraction of biomass, while the remainder derives from the alcohol co-reactant.

2.6.2.4 Space-time yield (STY)

$$STY\ (gL^{-1}h^{-1}) = \frac{Product\ (g)}{Reactor\ volume\ (L) \times Time\ (h)} \quad (7)$$

Space-time yield quantifies the mass of product generated per unit reactor volume per unit time. It is a critical engineering metric for process intensification and techno-economic

assessment, as higher values reduce reactor size requirements and capital costs [153, 155]. Space-time yield is therefore particularly valuable for catalytic processes such as alcoholysis, where it provides the most direct link between laboratory-scale performance and industrial feasibility.

2.6.2.5 Energy yield (%)

$$\text{Energy yield (\%)} = \frac{\text{Energy of products}}{\text{Energy of feedstock}} \times 100 \quad (8)$$

Energy yield is primarily employed in thermochemical processes, though expressed differently depending on the system. In gasification it is typically reported as cold gas efficiency, in combustion as thermal efficiency, and in hydrothermal liquefaction as energy recovery [67, 154, 160]. In this thesis, energy yields are not reported for alcoholysis due to the absence of reliable heating value data for alkyl levulinates, although this may become a valuable complementary metric once systematic combustion property data are available.

Together, these metrics provide complementary insights: mass yield reflects overall recovery, molar yield highlights molecular efficiency, carbon yield captures atom economy, space-time yield connects reaction chemistry to engineering productivity, and energy efficiency contextualises energy recovery in thermochemical systems.

2.6.3 Yield Representation in Thermochemical Conversion

Thermochemical conversion technologies operate at elevated temperatures and typically produce a broad distribution of products rather than a single dominant compound. As such, yield representation in these systems is distinct from catalytic or biochemical processes and often centres on bulk product recovery and energy efficiency rather than stoichiometric conversion.

2.6.3.1 Pyrolysis

Fast pyrolysis produces three main fractions: bio-oil, biochar, and non-condensable gases. Yields are usually expressed as the mass percentage of each fraction relative to the dry biomass input [161]. While this provides a simple mass balance, it obscures key aspects such as the oxygen content, heating value, and chemical stability of bio-oil, which strongly affect downstream upgrading potential [67]. For system-level analysis, energy yields are sometimes reported by allocating the feedstock's higher heating value (HHV) among the product fractions, enabling comparisons with other biofuel routes. However, because product quality varies widely with reactor type, heating rate, and temperature, mass yield alone is insufficient for meaningful process benchmarking.

2.6.3.2 Gasification

In gasification, the principal performance metric is the cold gas efficiency, which measures the ratio of chemical energy in the syngas to that in the input biomass [162, 163]. Additional metrics include specific syngas yield (Nm^3/kg biomass) and syngas composition, especially the H_2/CO ratio, which governs its suitability for Fischer–Tropsch synthesis, methanol production, or hydrogen-rich energy systems [154]. While cold gas efficiency is highly relevant for techno-economic assessments, it has limitations because it aggregates energy recovery without reflecting syngas composition. Two systems with identical cold gas efficiency can produce gases with very different downstream utility, underscoring the need to report multiple metrics in parallel.

2.6.3.3 Combustion

Combustion involves full oxidation of biomass to CO_2 and H_2O , and therefore yield is typically expressed in terms of thermal efficiency, the proportion of the feedstock's energy content converted into useful heat or power [164, 165]. Reported values depend on whether the higher heating value (HHV) or lower heating value (LHV) is used, as latent heat of vaporisation may or may not be recovered in practical systems. In some life-cycle assessment studies, exergy efficiency is also reported to account for the quality of energy

delivered. Although simple to calculate, thermal efficiency does not provide chemical insight and is better considered as an operational rather than a mechanistic performance metric.

2.6.3.4 Hydrothermal Liquefaction

Hydrothermal liquefaction converts wet biomass into a bio-crude oil under subcritical water conditions. The most widely reported metric is bio-crude mass yield (%), calculated relative to the dry biomass input [153, 166]. However, this metric can be misleading, since it does not reflect fuel quality or carbon allocation. To address this, studies increasingly report energy recovery (%), which incorporates the HHV of the bio-crude, and carbon and hydrogen recovery (%), which provide a clearer picture of the upgrading potential of the oil [167]. More recently, space-time yield has emerged as a critical metric in continuous hydrothermal liquefaction, linking throughput and kinetics to reactor design and economic feasibility. Nevertheless, challenges remain: laboratory-scale hydrothermal liquefaction studies often report high yields at low space-time yield, whereas commercial feasibility depends on achieving a balance between both.

In summary, yield representation in thermochemical conversion reflects the multi-product nature of these systems. Mass yields dominate in pyrolysis and hydrothermal liquefaction, cold gas efficiency and syngas composition are central to gasification, and thermal efficiency defines combustion performance. Yet each metric has inherent limitations: mass yields obscure product quality, cold gas efficiency masks gas composition, and thermal efficiency lacks chemical detail. The increasing use of complementary measures such as carbon recovery and space-time yield highlights the importance of a multi-metric approach. Compared to alcoholysis, which is a targeted liquid-phase catalytic process, thermochemical systems demonstrate how yield representation must adapt to the scale, purpose, and product complexity of each technology.

2.6.4 Yield Representation in Biochemical Conversion

Biochemical pathways employ enzymatic or microbial systems to transform biomass into fuels and chemicals. In contrast to thermochemical conversion, these processes typically aim to maximise the selectivity of a single product, such as ethanol or methane. Yield representation therefore centres on stoichiometric efficiency and volumetric productivity, but challenges arise due to feedstock heterogeneity, inhibitory by-products, and process integration.

2.6.4.1 Fermentation

Fermentation converts monosaccharides and polysaccharide hydrolysates into ethanol, organic acids, or other bioproducts. The most widely used metric is molar yield (%), expressed as moles of product per mole of sugar consumed [152, 168]. For ethanol fermentation by *Saccharomyces cerevisiae*, the theoretical maximum is ~0.51 g ethanol per g glucose (~90–95% of the stoichiometric limit), deviations from which indicate inefficiencies such as by-product formation or incomplete sugar utilisation [169]. Complementary metrics include volumetric productivity ($\text{g L}^{-1} \text{ h}^{-1}$) and space-time yield, both of which capture the reactor's throughput and are crucial for techno-economic analysis. However, comparisons between studies are often complicated by differences in hydrolysate composition, pretreatment severity, and microbial tolerance to inhibitors. Thus, while molar yield provides a chemically rigorous measure of efficiency, it must be contextualised alongside productivity metrics to capture industrial relevance.

2.6.4.2 Anaerobic Digestion

In anaerobic digestion, yield is typically reported as biogas volume per unit substrate, often in m^3 of biogas per tonne of volatile solids or per kilogram of chemical oxygen demand removed [154]. Because methane content (typically 50–70%) governs energy value, specific methane yield is increasingly reported as the key metric for life-cycle and techno-economic assessment [170]. While simple volume-based metrics provide useful comparability, they can mask differences in gas composition, retention time, and feedstock degradability. For example, high yields from manure and sewage sludge may not be directly comparable to

those from lignocellulosic residues without accounting for the fraction of biodegradable carbon [171]. Moreover, productivity measures such as methane production rate ($\text{L CH}_4/\text{L reactor/day}$) are critical when comparing high-rate systems like upflow anaerobic sludge blanket reactors with low-rate digesters. In practice, no single yield metric fully describes anaerobic digestion performance, and a suite of volumetric, compositional, and productivity indicators is required.

2.6.4.3 Enzymatic Hydrolysis

Enzymatic hydrolysis catalyses the depolymerisation of cellulose and hemicellulose into fermentable sugars. Yields are typically expressed as glucose conversion (%) relative to the theoretical maximum based on the stoichiometry of cellulose hydrolysis [155]. This is sometimes reported on a mass basis ($\text{g glucose/g cellulose}$) or as a molar conversion ($\text{mol glucose/mol anhydroglucose unit}$). While conceptually simple, yields are often limited by substrate crystallinity, lignin content, enzyme inhibition, and product feedback inhibition [172]. To better capture process performance, researchers increasingly report space-time yield and volumetric productivity, especially in high-solids hydrolysis or integrated simultaneous saccharification and fermentation (SSF) systems [173]. These metrics are more relevant for scale-up, as they link enzyme kinetics to reactor throughput. However, reporting remains inconsistent, with some studies focusing solely on final sugar yields while omitting productivity data, making it difficult to benchmark enzymatic systems fairly.

Biochemical yield metrics reflect the molecular precision of enzymatic and microbial transformations, but they also expose significant challenges in standardisation. Molar yields are theoretically rigorous but depend on precise substrate definition, which is often difficult with complex lignocellulosic feedstocks. Productivity metrics such as space-time yield and volumetric productivity are better aligned with industrial needs but are still inconsistently reported. Anaerobic digestion highlights the additional challenge that volume-based yields may obscure compositional and kinetic differences. Taken together, biochemical systems demonstrate the importance of reporting multiple complementary yield metrics, molecular efficiency (molar yield), feedstock utilisation (conversion %), and reactor productivity

(space-time yield), to provide a comprehensive and comparable picture of process performance.

2.6.5 Yield Representation in Chemical Conversion

Chemical conversion processes such as alcoholysis, hydrolysis, esterification, and transesterification are widely applied in biomass valorisation. Unlike thermochemical pathways that generate a wide distribution of products, these catalytic liquid-phase systems target specific molecules such as alkyl levulinates, levulinic acid, or fatty acid esters. Yield representation therefore focuses on molecular efficiency and reactor productivity.

2.6.5.1 Alcoholysis

Alcoholysis is distinct among chemical conversion technologies in that the solvent also acts as a reactant, producing alkyl levulinates alongside dialkyl ether and ester co-products. Traditionally, yields in alcoholysis have been reported as molar yield values calculated only with respect to cellulose [116, 120]. However, this method systematically overestimates efficiency, as it neglects the contribution of hemicellulose to alkyl levulinate formation [44, 124]. This thesis demonstrates that hemicellulose-derived sugars also contribute significantly, meaning yields based only on cellulose misrepresent both molecular efficiency and process selectivity. The application of this method is shown in Section 2.6 (Figure 14 and Table 2), where reported yields of n-butyl levulinate were recalculated using this approach, providing a more realistic representation of molecular efficiency.

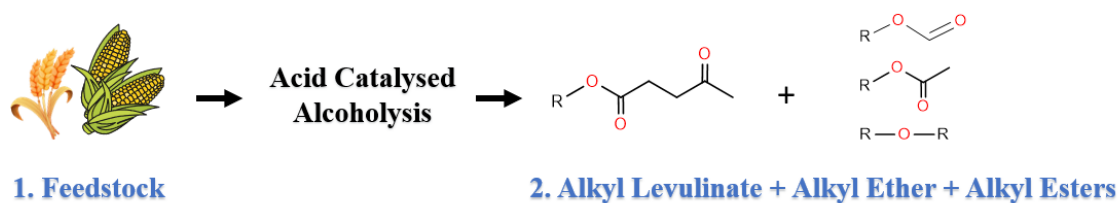


Figure 15. Schematic of acid-catalysed alcoholysis of lignocellulosic biomass. In a single step, the carbohydrate fraction of the feedstock is directly converted into alkyl levulinate, accompanied by ethers and alkyl esters as co-products. Alcohol acts simultaneously as solvent and reactant, making alcoholysis a one-pot route to biofuels.

This effect is clearly illustrated in Figure 16 which compares molar yields of n-butyl levulinate for different lignocellulosic feedstocks when expressed relative to cellulose alone or to the combined cellulose and hemicellulose content. The recalculated values show that including hemicellulose significantly lowers the apparent efficiency, providing a more realistic assessment of molecular performance. This comparison highlights how the choice of yield normalisation framework strongly influences reported outcomes and underlines the need for consistent and transparent methods when benchmarking catalytic systems.

In addition to molar yield, mass yield is often reported, particularly when raw biomass feedstocks are used [106, 121]. While straightforward and widely applicable, mass yield fails to capture the partitioning of carbon from alcohol co-reactants. A more transparent representation is carbon yield, which tracks the proportion of carbon atoms from the biomass incorporated into the desired product compared to those diverted into humins, ethers, or gaseous by-products. This approach aligns with life-cycle analysis and provides a direct link to carbon efficiency.

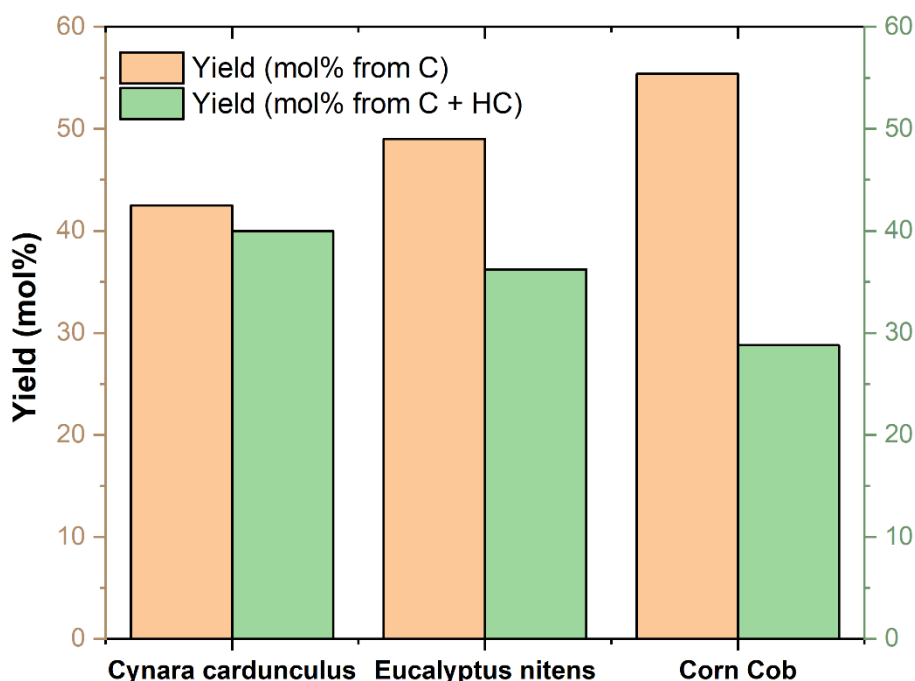


Figure 16. Comparison of molar yields for the butanolysis of lignocellulosic biomass expressed relative to cellulose alone (C) and to the combined cellulose and hemicellulose content (C + HC). Data are shown for *Cynara cardunculus* [121], *Eucalyptus nitens*, and corn cob, illustrating the influence of yield normalisation framework on reported performance.

Finally, space-time yield, expressed in grams of product per litre of reactor volume per hour, has emerged as a critical metric for alcoholysis, particularly in techno-economic assessment and scale-up studies [153]. Space-time yield captures volumetric productivity, reflecting both catalytic activity and reactor design. For example, increasing alcoholysis temperature can enhance space-time yield by accelerating reaction kinetics, even if molar yield remains unchanged. As such, space-time yield provides the most direct link between laboratory-scale catalyst testing and industrial feasibility.

2.6.5.2 Hydrolysis and Esterification

In acid- or base-catalysed systems, hydrolysis of carbohydrates produces levulinic acid, which must then undergo a subsequent esterification step with an alcohol to generate alkyl levulinates [172]. This two-step pathway contrasts with alcoholysis, which achieves both transformations in a single pot, making it a quicker and more atom-economical route to biofuels. The same considerations regarding yield apply across these processes: molar yield is the most common measure but can be misleading if not normalised to the correct biomass fractions, while mass yield, carbon yield, and space-time yield provide complementary perspectives on efficiency and scalability. Thus, although hydrolysis and esterification are mechanistically distinct from alcoholysis, their yield representation follows the same principles, with alcoholysis offering the advantage of higher process efficiency through direct ester formation.



Figure 17. Schematic of the two-step hydrolysis–esterification pathway for producing alkyl levulinates from lignocellulosic biomass. Carbohydrates are first converted to levulinic acid via acid-catalysed hydrolysis, followed by esterification with an alcohol to yield the target alkyl levulinate. This route requires sequential processing, making it slower and less atom-economical than alcoholysis.

2.6.5.3 Transesterification

Biodiesel production via transesterification of triglycerides with short-chain alcohols is generally reported as mass yield, calculated as the proportion of fatty acid alkyl esters obtained relative to the oil feedstock [157]. This convention reflects established biodiesel

fuel standards, which specify ester content, viscosity, and stability. In catalyst development and process intensification studies, however, space-time yield is increasingly reported to quantify reactor productivity, particularly in continuous-flow systems where volumetric throughput is critical [174]. This convention reflects established biodiesel fuel standards, which specify ester content, viscosity, and stability. In catalyst development and process intensification studies, however, space-time yield is increasingly reported to quantify reactor productivity, particularly in continuous-flow systems where volumetric throughput is critical

2.6.5.4 Catalytic Hydrogenation and Upgrading

Hydrogenation processes that convert levulinic acid, furfural, or hydroxymethylfurfural into higher-value fuels and chemicals are usually assessed using molar yield, selectivity, and space-time yield [175-177]. Selectivity is particularly important in these systems due to competing hydrogenolysis and polymerisation reactions, while space-time yield provides an economic measure of catalyst performance in continuous reactors. These upgrading reactions are central to the development of sustainable aviation fuels and biobased chemicals, underscoring the need for consistent reporting of both molecular efficiency and reactor productivity.

Chemical conversion technologies demonstrate both the strengths and the limitations of yield representation in targeted catalytic systems. Molar yield remains the most common metric but can be misleading without a clear definition of the substrate basis. Mass yield is accessible but chemically incomplete, while carbon yield offers a more transparent view of carbon efficiency. Space-time yield is the metric most closely tied to industrial scale-up and process economics and should therefore be reported alongside molecular yields. In alcoholysis specifically, the introduction of combined cellulose–hemicellulose molar yields and carbon yield frameworks provides a more rigorous and reproducible foundation for comparing catalytic systems.

2.6.6 Challenges and Misrepresentations in Yield Reporting

Despite the centrality of yield in biomass conversion research, its representation is often inconsistent, incomplete, or misleading. These issues arise from differences in feedstock complexity, process objectives, and methodological assumptions, which together make it difficult to compare results across studies or technologies.

In thermochemical systems, yields are usually reported as mass fractions of oil, char, and gas, or as energy efficiency. While simple, these measures obscure product quality. For instance, two pyrolysis oils may have identical mass yields but very different oxygen contents and heating values, leading to divergent upgrading requirements. Similarly, cold gas efficiency in gasification aggregates energy recovery but conceals the influence of syngas composition, particularly the hydrogen-to-carbon monoxide ratio that dictates suitability for downstream synthesis.

In biochemical systems, molar yield is rigorous when pure sugars are used but becomes problematic with lignocellulosic feedstocks. Variation in cellulose, hemicellulose, and lignin composition complicates normalisation, and inhibitory by-products often reduce volumetric productivity but are not consistently reported. Anaerobic digestion highlights another challenge: reporting biogas volume without methane content can exaggerate energy potential.

In catalytic chemical conversions, yield misrepresentation is especially evident in alcoholysis. Conventional molar yields calculated only from cellulose systematically overestimate efficiency, as they neglect hemicellulose contributions. This inflates perceptions of catalyst selectivity and process performance. A related issue arises in hydrolysis and esterification, where levulinic acid and esterification yields are often reported separately, complicating comparisons with the one-pot alcoholysis pathway. Even in mature technologies such as biodiesel transesterification, mass yield alone can obscure reactor productivity, which is better captured by space-time yield. In alcoholysis specifically, the omission of side-products such as humins and dialkyl ethers further undermines transparency, leaving carbon balances incomplete and reported efficiencies overstated.

Across all technologies, selective omission of side-products such as humins, ethers, organic acids, and gases further undermines transparency, often leaving carbon balances incomplete and efficiency overstated. The absence of standardisation in whether yields are

reported on a mass, molar, carbon, or energy basis compounds these problems, creating barriers to comparability and hindering robust assessment.

In summary, yield misrepresentation is not an isolated issue but a systemic problem across biomass conversion. Whether through incomplete balances, inappropriate normalisation, or selective reporting, inconsistent yield definitions obscure the link between laboratory-scale results and industrial feasibility, undermining both techno-economic analysis and life-cycle assessment.

2.6.7 Towards Standardised Yield Reporting

The diversity of biomass conversion pathways means that no single yield metric can adequately capture both molecular efficiency and process productivity. Thermochemical systems are best represented through mass and energy balances, biochemical systems rely on molar yields and productivity measures, and catalytic chemical conversions require a combination of molecular and engineering perspectives. This variability has led to inconsistent reporting practices that hinder comparison across studies and complicate techno-economic analysis and life-cycle assessment.

A way forward is to adopt a multi-metric framework for yield reporting. For catalytic processes such as alcoholysis, this should include:

- Molar yield, to quantify stoichiometric efficiency and benchmark catalyst selectivity.
- Mass yield, to provide a straightforward measure of overall product recovery from raw biomass.
- Carbon yield, to track atom economy and carbon allocation between desired products, co-products, and by-products such as humins.
- Space-time yield, to link chemical efficiency with reactor throughput and industrial feasibility.

Alongside these molecular and engineering indicators, energy yield remains an essential metric in thermochemical systems. Reporting the distribution of the feedstock's heating value across gas, liquid, and solid fractions is central to both techno-economic and life-cycle assessments. Although energy yield is not calculated here for alcoholysis due to the absence of reliable heating value data for alkyl levulinates, this reflects a limitation in the field rather than a lack of relevance. As combustion property data for levulinates become more

Chapter 2. Literature Review of Alcoholysis

systematically available, energy yield may emerge as a valuable complementary measure for benchmarking alcoholysis against other biomass conversion pathways.

Table 4 summarises the dominant yield metrics across major biomass conversion technologies. It highlights the diversity of approaches, the specific terminology used in different systems, and the need for a consistent multi-metric framework to ensure fair comparison.

Table 4. Dominant yield metrics across biomass conversion technologies

Conversion Method	Primary Yield Metric(s)	Notes
Thermochemical Conversion		
Pyrolysis	Mass yield (%); Energy yield (%)	Mass yield reported for oil, char, and gas fractions; energy yield used for system-level efficiency [67, 161].
Gasification	Cold gas efficiency (%); Gas yield (Nm ³ /kg biomass); Syngas composition	Cold gas efficiency measures overall energy recovery; syngas composition, especially H ₂ /CO ratio, governs suitability for downstream synthesis [162, 163].
Combustion	Thermal efficiency (%); Exergy efficiency (%)	Thermal efficiency based on higher or lower heating value; exergy sometimes used for quality-adjusted comparisons [164, 165].
Hydrothermal Liquefaction	Mass yield (%); Energy recovery (%); Space-time yield	Mass yield common in batch studies; energy recovery reflects product quality; space-time yield increasingly reported in continuous reactors [153, 166].
Biochemical Conversion		
Fermentation	Molar yield (%); Space-time yield	Molar yield reflects stoichiometric efficiency; productivity metrics critical for scale-up [152].
Anaerobic Digestion	Biogas yield (m ³ /kg volatile solids); Methane content (%)	Biogas volume indicates conversion; methane content defines energy value; [154, 171].
Enzymatic Hydrolysis	Glucose yield (%); Mass yield (g/g cellulose); Space-time yield	Expressed as cellulose or hemicellulose conversion; productivity metrics valuable in high-solids and integrated processes [155, 173].
Chemical Conversion		
Alcoholysis	Molar yield (%); Mass yield (%); Carbon yield (%); Space-time yield	One-pot route to alkyl levulinates; carbon yield provides transparent carbon allocation; space-time yield links to techno-economic feasibility [44, 121].
Hydrolysis & Esterification	Molar yield (%); Selectivity (%); Space-time yield	Two-step route via levulinic acid; yield representation similar to alcoholysis but less atom-efficient [63, 178].
Transesterification	Mass yield (%); Space-time yield	Mass yield aligns with biodiesel standards; space-time yield used in catalyst development and continuous-flow systems [157, 174].
Catalytic Hydrogenation & Upgrading	Molar yield (%); Selectivity (%); Space-time yield	Selectivity critical due to competing reactions; space-time yield essential for continuous reactor benchmarking [175-177].

In conclusion, yield must be represented not as a single number but as a suite of complementary indicators. Standardising the use of mass, molar, carbon, space-time, and energy yields across biomass conversion technologies is not simply desirable but essential. Only by adopting this framework can researchers generate data that are directly comparable, robust for techno-economic modelling, and meaningful in life-cycle analysis. For alcoholysis in particular, such standardisation provides a rigorous basis for benchmarking

against alternative pathways and highlights its potential as a one-pot route to advanced biofuels.

2.7 Critical Perspective

In summary, alcoholysis provides a uniquely simple and effective route to alkyl levulinates, offering one pot conversion, solvent–reactant synergy, and the generation of valuable ether and ester coproducts. Yet the literature remains fragmented: levulinate yields are frequently overstated due to cellulose only normalisation, coproducts such as ethers, formates, and acetates are inconsistently reported, and humin formation is poorly characterised. Kinetic modelling studies are exceptionally scarce, with only a handful available for ethanolysis and none for butanolysis, and even these models are limited in scope, undermining mechanistic understanding and predictive reliability. While ethanolysis has been comparatively well studied, butanolysis and real biomass systems remain underexplored, with systematic comparative data largely absent. This thesis directly addresses these shortcomings by developing a rigorous yield framework and comprehensive product accounting, providing a more accurate and comparable basis for evaluating alcoholysis as a pathway to advanced biofuels.

Chapter 3

Methodology

3.1 Overview of Experimental Framework

The experimental programme was designed to investigate the alcoholysis of representative carbohydrate feedstocks for the production of alkyl levulinates, with an emphasis on reproducibility, comparability across feedstocks, and methodological robustness. Alcoholysis was selected as the central conversion route due to its dual advantage of effective carbohydrate depolymerisation and in situ esterification of levulinic acid, thus generating alkyl levulinates directly. This approach aligns with prior reports highlighting alcoholysis as a promising pathway for advanced biofuel synthesis, combining high yields with favourable process integration potential.

Two alcohols, ethanol and *n*-butanol, were chosen as solvents and esterifying agents. Ethanol was included given its widespread availability, compatibility with existing fuel infrastructures, and inclusion in RED II/RED III Annex IX feedstock-based processes. *n*-Butanol was studied subsequently as a longer-chain analogue, offering enhanced miscibility with diesel fractions and improved fuel properties of the resulting esters. Importantly, both ethanol and *n*-butanol can be produced renewably from biomass, with ethanol typically derived through microbial fermentation of sugar- or starch-rich crops, and butanol produced via acetone–butanol–ethanol (ABE) fermentation or through engineered microbial pathways using lignocellulosic residues [179-181]. This dual-alcohol framework therefore not only provides a systematic basis for assessing reaction behaviour but also ensures that the products investigated remain aligned with sustainable and scalable biofuel strategies.

A shared methodological foundation was applied across all experiments, encompassing feedstock pre-treatment, reaction setup, neutralisation, and analytical protocols. Within this framework, two distinct alcoholysis methods were employed: (i) a pressure-tube configuration optimised for reactions up to 150 °C, and (ii) a polytetrafluoroethylene (PTFE) lined autoclave system enabling reactions at 170–210 °C with improved robustness and reproducibility. Both methods converged on a common analytical workflow, including gas chromatography for yield determination, elemental analysis for elemental characterisation, and nuclear magnetic resonance spectroscopy for structural elucidation.

This experimental design ensures consistency in comparative analyses while also allowing exploration of process variables across a relevant temperature range and with two industrially significant, renewably producible alcohols.

3.2 Experimental Materials and Preparation

3.2.1 Feedstock Procurement and Pre-treatment

Corn cobs cleaned of their kernels have become an important reference biomass for advanced biofuel applications. Thus, this study utilizes it as a typical real-world lignocellulosic biomass, compatible with RED II/RED III Annex IX [27]. Steamed corn on the cob was purchased from a local supermarket and washed to remove any non-lignocellulosic mass. The corn kernels were removed, and the cob was sliced into ≈ 2.5 cm pieces. The pieces were weighed and then dried over several days in an oven at 70 °C until no further mass loss was observed. The dried corn cobs were then mechanically broken into smaller pieces and ball-milled for 2 hours. The milling was done using a Glen Creston Spex 8000 mixer/mill with stainless steel balls characterized by a powder charge ratio of 15:1. The resulting powdered corn cob was sieved using a Retsch mesh sieve to isolate and then collect corn cobs of 100–125 μm . These particles were subsequently stored under vacuum in a desiccator until use. For consistency, the D-(+)-glucose and cellulose feedstocks were also sieved to a particle size of 100–125 μm .

3.2.2 Reagents and Solvents

All materials were purchased from commercial suppliers and used without further purification unless stated otherwise. Ethanol ($\geq 99.8\%$), *n*-butanol ($\geq 99.8\%$), ethyl levulinate (99 %), *n*-butyl levulinate (99 %), *n*-butyl formate ($\geq 99\%$), *n*-butyl acetate ($\geq 99\%$), furfural ($\geq 99\%$), sulphuric acid (95–97 %), anhydrous dimethyl sulfoxide (DMSO) ($\geq 99.9\%$), diethyl ether ($\geq 99.8\%$), and di-*n*-butyl ether ($\geq 99.8\%$) were purchased from Sigma-Aldrich. Anhydrous D-(+)-glucose (99 %) and microcrystalline cellulose were purchased from Alfa Aesar. Sodium hydrogen carbonate ($\geq 99.7\%$) was purchased from Fisher Scientific. Metal autoclaves and 25 mL PTFE liners were obtained from Xiamen CRTOP Machine Co., Ltd., and 15 mL pressure vessels were purchased from Ace Glass,

3.3 Alcoholysis Methods

Two methodologies were employed for the alcoholysis of carbohydrate feedstocks to produce alkyl levulinates. The first approach was adapted from earlier work within the

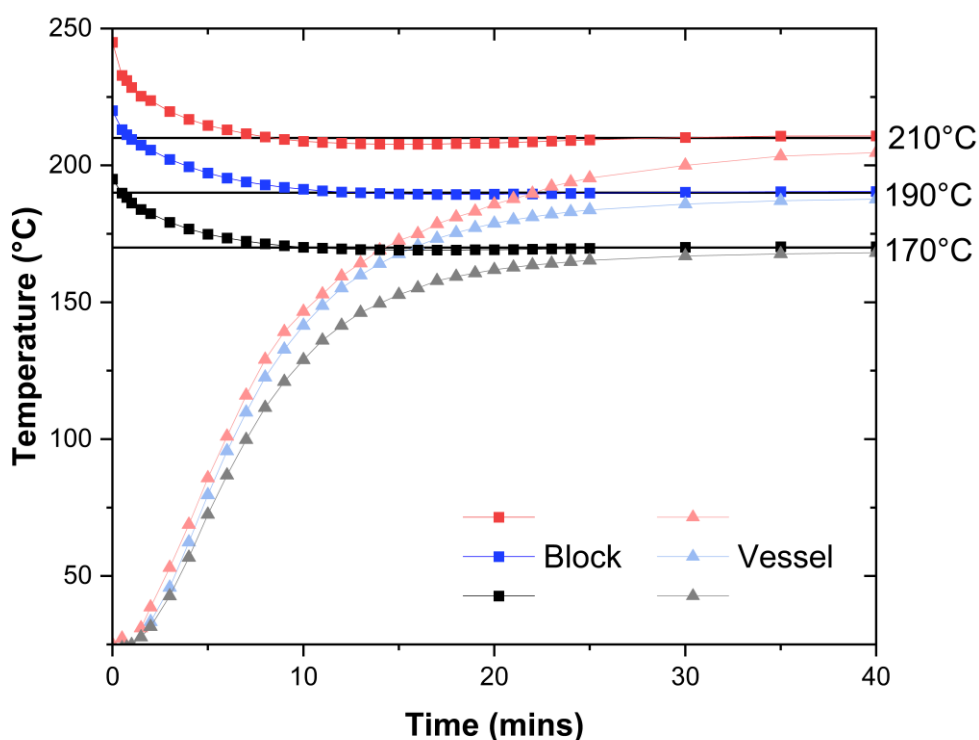


Figure 18. Heating profile of aluminium blocks and reaction vessels (PTFE liners in stainless steel autoclave reactors) used for alcoholysis experiments. Blocks were pre-heated to 25–35 °C above the target temperature and allowed to equilibrate to the desired setpoint upon insertion of the experimental vessels.

research group [51, 61], where preliminary optimisation studies had established a reliable procedure for reactions at temperatures up to 150 °C. However, the need to conduct experiments at higher temperatures (up to 210 °C) necessitated the development of a revised reactor system.

The key modifications involved both the heating blocks and the reactor vessels. Conventional pressure tubes were replaced with PTFE liners enclosed within stainless steel autoclaves, providing greater robustness, reduced gas loss through leakage, and significantly improved safety. This configuration allowed reactions to be performed reproducibly at elevated temperatures without the risks of cracking or explosion associated with glass pressure tubes. Owing to these advantages, the autoclave-based method is recommended for future alcoholysis studies.

The new system also required adjustments to heating protocols. Because of the higher thermal mass of the stainless steel autoclaves, the standard aluminium heating blocks exhibited insufficient heat capacity to rapidly achieve the target reaction temperature. To compensate, no more than eight reactors were loaded per block (total capacity of 16), while the remaining slots were filled with solid aluminium inserts to increase the block's heat capacity. The heating blocks were then preheated to 25–35 °C above the desired setpoint to ensure rapid equilibration of the reactors. This ensured efficient equilibration of the vessels to the intended temperature, as confirmed by recorded temperature profiles of the blocks and reactors (Figure 18). Reaction time was defined as commencing at the point when the reactor vessel was introduced into the preheated block.

3.3.1 Alcoholysis Procedure – Method A

Feedstock, alcohol, and sulphuric acid were added to a 15 mL pressure tube with a magnetic stirrer. The total mass of the three reactants was set at 5 grams, and the percentage mass of each reactant was adjusted according to the desired reaction conditions. The pressure tube was tightly sealed and placed in an insulated aluminium heating block at 150 °C for the desired reaction time. The heating block was insulated with a 2.5 cm layer of Styrofoam covered with tin foil that enclosed all sides of the block. After completion, the pressure tube was placed in a teflon rack and air-cooled to guarantee that the contents returned to the condensed phase.

Once cooled, the reaction mixture was centrifuged at 5500 rpm for 5 minutes (Benchmark LC-8 centrifuge). Following the separation of the supernatant, the reactions were neutralised by adding an excess of sodium hydrogen carbonate (NaHCO_3 , 50 mg) to prevent potential damage to the gas chromatography column from residual acidity in the solution. An aliquot of the reaction mixture (250 mg) was diluted in dimethyl sulfoxide to achieve a mass ratio of solvent to reaction mixture of 400:1.



Figure 19. Overview of the nine-stage experimental workflow, from biomass preprocessing and milling through reaction preparation, reaction run, cooling, centrifugation, and sample preparation, concluding with product quantification by gas chromatography.

3.3.2 Alcoholysis Procedure – Method B

Feedstock, alcohol, and sulphuric acid (total mass 5 g) were added to a 20 mL PTFE liner equipped with a magnetic stirrer. The controlled reaction variables were temperature (170–210 °C) and time (0.5–5 h). Each PTFE liner was placed into a stainless steel autoclave, which was then positioned in an aluminium heating block. To ensure rapid equilibration of the reactors, the heating blocks were preheated to 25–35 °C above the desired setpoint, allowing the reactors to reach the target temperature efficiently once inserted. After the prescribed reaction time, the autoclaves were removed from the heating block and allowed to cool to room temperature in air.

Once cooled, the reaction mixtures were centrifuged at 5500 rpm for 5 minutes (Benchmark LC-8 centrifuge). Following separation of the supernatant, residual acidity was neutralised by the addition of sodium hydrogen carbonate (NaHCO_3 , 50 mg). The bicarbonate reacts with sulphuric acid and organic acids present in the mixture, releasing CO_2 gas and forming sodium sulphate and sodium carboxylate salts. These salts are poorly soluble in the predominantly organic medium and therefore precipitate out of solution. An aliquot of the neutralised supernatant (250 mg) was then diluted in dimethyl sulfoxide (DMSO) to achieve a solvent-to-sample mass ratio of 400:1.

3.4 Analytical Techniques

3.4.1 Gas Chromatography (GC-FID)

Following neutralisation, aliquots of the liquid-phase reaction mixtures were sampled and analysed by gas chromatography (GC). Sample preparation was performed on a gravimetric basis: 500 mg of reaction mixture was diluted in dimethyl sulfoxide (DMSO) at a solvent-to-sample mass ratio of 400:1, with the precise mass of DMSO recorded in each case. DMSO was selected as the diluent owing to its exceptional solvating power for both polar and non-polar components. This ensured comprehensive dissolution of the diverse products and by-products formed during alcoholysis, including viscous fractions, thereby preventing incomplete solubilisation and reducing the risk of column damage or blockages in the GC system.

Then, the solution was transferred to a crimp top vial for GC analysis. Such an analysis was performed on a Perkin Elmer Clarus 580, GC-FID, equipped with an Agilent DB-624 column (30 m, 320 μm i.d., 1.80 μm film) using the TotalChrom 6.3.2 software package (MA, USA). Hydrogen was used as the carrier gas, with a constant flow of 2 mL/min. The inlet temperature was maintained at 493.15 K with the detector set to 543.15 K. A sample volume of 1 μL was injected at a split of 40:1. The oven conditions were: 348.15 K for 2 minutes, 10 K/min to 423.15 K; 20 K/min to 443.15 K, 10 K/min to 493.15 K.

3.4.2 Elemental (CHNOS) Analysis

Elemental composition of feedstocks and solid residues was determined using an Elementar EL Cube analyser. Carbon, hydrogen, nitrogen, sulphur, and oxygen contents were measured directly, with all analyses performed in duplicate and reported as averages.

For C, H, N, and S determination, samples were weighed into silver boats and combusted under oxygen at 950 °C, and the resulting gases were quantified by a thermal conductivity detector (TCD). For oxygen quantification, samples were also weighed into silver boats and pyrolysed at 1150 °C in O-mode, where oxygen was converted to CO in the presence of a carbon catalyst and subsequently detected by TCD. Calibration was carried out using benzoic acid as a reference standard.

This method provides direct measurement of oxygen content, avoiding the common practice of calculating oxygen by difference, and thus improves the accuracy and reliability of ultimate analysis for both lignocellulosic feedstocks and humin residues.

3.4.3 Biochemical Analysis of Biomass

Biochemical analysis of dried ground corn cob was performed by Celignis Analytical according to the National Renewable Energy Laboratory (NREL) procedure for determining structural carbohydrates and lignin in biomass [182]. The extractives were removed (Dionex ASE-200), and the water-soluble extractives were analysed for sugars. Acid hydrolysis was carried out, and the hydrolysates were analysed on an ion chromatograph (Dionex ICS-3000) to determine the cellulose and hemicellulose content. The hydrolysates were analysed using ultraviolet-visible spectrophotometry (HP 8452A) to determine the acid-soluble lignin content. After that, the hydrolysis residues were calcined at $(575 \pm 25)^{\circ}\text{C}$ to determine the Klason Lignin content. In addition, the ash contents were measured after calcination at $(575 \pm 25)^{\circ}\text{C}$ for (24 ± 6) hrs, at a heating rate of $10^{\circ}\text{C}/\text{min}$ using a Nabertherm furnace.

3.4.4 Nuclear Magnetic Resonance (NMR) Determination of Degree of Acetylation

3.4.4.1 Nuclear Magnetic Resonance Analysis

Nuclear magnetic resonance spectroscopy was employed to determine the degree of acetylation of xylan isolated from corn core, a feedstock investigated in this study. ^1H NMR enables differentiation between two key proton environments associated with the degree of acetylation: hydroxyl (OH) protons and the methyl protons of acetyl groups (CH_3). For each acetylated monomer unit in xylan, an OH moiety is substituted by an acetyl CH_3 group. Thus, the relative abundance of these proton types provides a basis for quantifying the degree of acetylation.

The degree of acetylation may be expressed in two forms (i) location-based, describing the proportion of hydroxyl groups substituted by acetyl groups, and (ii) monomer-based, indicating the average number of acetyl groups per monomer. Both metrics are reported herein.

Approximately 1.0 g of xylan was dried in a vacuum oven at 60 °C for 24 hrs prior to analysis. NMR tubes (5 mm thin wall, 7", Fluorochem EU Ltd.) and their respective caps were similarly dried. Samples were prepared using 0.20 g xylan dissolved in 0.80 g of DMSO-d_6 without the use of a paramagnetic relaxation agent. Spectra were acquired on a Bruker Avance III 400 MHz instrument under the conditions listed in Table 5.

3.4.4.2 Location-Based Degree of Acetylation

The location-based degree of acetylation was calculated as the ratio of the acetyl CH_3 signal intensity to the combined intensity of the acetyl CH_3 and hydroxyl (OH) signals according to Equation 9:

$$\text{Location – based degree of acetylation} = \frac{CH_3^{acetyl}}{CH_3^{acetyl} + OH^{total}} \quad (9)$$

where CH_3^{acetyl} is the relative concentration of acetyl CH_3 groups, and OH^{total} is the total relative concentration of hydroxyls.

Table 5. Experimental parameters used to acquire ^1H NMR spectra to determine the degree of acetylation of xylan.

Parameter	Units	Value
Solvent	-	DMSO-d ₆
Solvent Mass	g	0.80
Sample Mass	g	0.20
[Cr(acac) ₃]	M	0
Field Strength	MHz	400
Flip Angle	°	90
Acquisition Time	s	4
Delay Time	s	60
Time Domain Points	x10 ³	64
Sweep Width	Hz	8012
Dwell Time	μs	62.4
Scans	-	16
Line Broadening	Hz	0.3

3.4.4.3 Monomer-Based Degree of Acetylation

To express the degree of acetylation on a monomer basis, two assumptions were made:

1. Each xylose monomer contains either zero or one acetyl substituent.
2. Acetylation accounts for all non-saccharide substituents in the xylan structure.

Assumption (2) is supported by the absence of non-acetyl signals in the NMR spectra. Arabinose, a potential side-chain sugar, would yield overlapping signals with xylose and thus would not affect the validity of the acetylation calculation.

Under assumption (1), each acetyl group corresponds to a monoacetylated monomer bearing one less hydroxyl group. Conversely, unacetylated monomers contain two free OH groups. The relative concentration of unacetylated monomers was therefore calculated as:

$$\text{Relative concentration of unacetylated monomers} = M_u = \frac{OH^{total} - CH_3^{acetyl}}{2} \quad (10)$$

Accordingly, the monomer-based degree of acetylation was calculated as:

$$\text{Monomer – based degree of acetylation} = \frac{CH_3^{acetyl}}{M_u + CH_3^{acetyl}} \quad (11)$$

This approach enables accurate quantification of xylan acetylation using simple integrals from ^1H NMR spectra.

3.5 Data Processing and Uncertainties

3.5.1 Experimental rigour

For each set of reaction conditions, two independent experiments were performed. Each reaction mixture was then analysed in duplicate by gas chromatography (technical replicates), resulting in a total of four data points per condition. Reported uncertainties correspond to the standard deviation of these four measurements. For steady-state concentrations and yields, the uncertainties were calculated from the subset of data points meeting the steady-state criteria described in Section 3.6.1.

3.5.2 Yield Calculation

Yields from ethanolysis and butanolysis experiments were calculated using multiple approaches to ensure consistency across different feedstocks and to enable mass, molar, and carbon balances. The following definitions were applied.

3.5.2.1 Mass Yield

The percentage mass yield of alkyl levulinate relative to the initial biomass was calculated according to Equation 12:

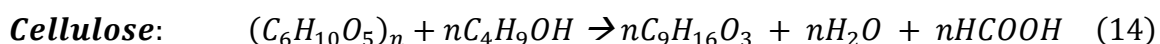
$$\text{Yield (wt. \%)} = \frac{\text{Alkyl levulinate (g)}}{\text{Biomass (g)}} \times 100 \quad (12)$$

This provides the mass efficiency of biomass-to-product conversion.

3.5.2.2 Molar Yield

The molar yield of alkyl levulinate was calculated relative to the maximum theoretical yield obtainable from cellulose and hemicellulose, as defined in Equations 14 and 15, using the butanolysis of cellulose and xylan to butyl levulinate as examples.

$$\text{Yield (mol\%)} = \frac{\text{Alkyl levulinate (mol)}}{\text{Max. yield from cellulose and hemicellulose (mol)}} \times 100 \quad (13)$$



Equation 15 balances the contribution of hemicellulose by representing it as an idealised polyxylose chain, where the 1.2 stoichiometric factor accounts for the different carbon-to-oxygen ratio relative to cellulose. This approximation enables a consistent basis for comparing theoretical levulinate yields across feedstocks containing both cellulose and hemicellulose.

3.5.2.3 Carbon Yield

The carbon-based yield was calculated to monitor carbon allocation during alcoholysis, with Equation 16 illustrating the case of butanolysis for the production of butyl levulinate (BL).

$$\text{Carbon Yield (mol\%)} = \frac{\text{Moles of C formed as BL}}{\text{Max moles of C converted to BL}} = \frac{\text{BL (g)} \times \text{C in BL (wt.\%)}}{\left(\frac{9}{5}\right) \times \text{Feedstock (g)} \times \text{C in Feedstock (wt.\%)}} \quad (16)$$

Here, the factor 9/5 accounts for the contribution of five carbon atoms from the carbohydrate fraction and four from butanol.

3.5.2.4 Space-Time Yield (STY)

To assess productivity, the space-time yield was calculated as the mass of product formed per unit reactor volume per unit time, based on the time to 90% of the predicted maximum yield (T_{90}), which also corresponds to our definition of the steady-state:

$$STY (gL^{-1}h^{-1}) = \frac{\text{Alkyl levulinate at } T_{90} (g)}{\text{Reactor volume } (L) \times T_{90} (h)} \quad (17)$$

3.6 Thermodynamic Considerations

3.6.1 Steady-state conditions

From a thermodynamic perspective, a reaction proceeds until the concentrations of reactants and products minimise the Gibbs free energy of the system:

$$\Delta G_0 = -RT \ln K_{eq} \quad (18)$$

where ΔG° is the standard Gibbs free energy, R is the universal gas constant, T is the absolute temperature (K), and K_{eq} is the equilibrium constant. The resulting equilibrium composition is a critical reference point for validating physics-based analyses, such as kinetic modelling, which must remain consistent with mass conservation and thermodynamic principles.

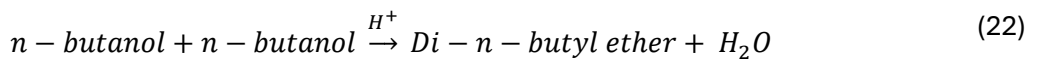
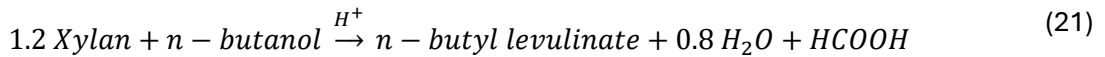
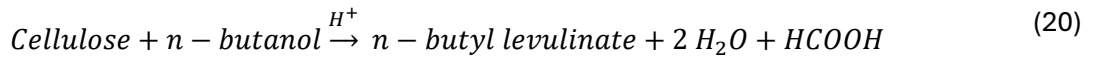
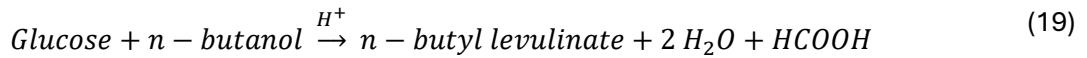
To characterise these equilibria experimentally, the masses of reactants, products, and co-products (e.g., *n*-butanol, *n*-butyl levulinate, di-*n*-butyl ether, *n*-butyl formate, *n*-butyl acetate, furfural, humins, and water) were quantified, as this determines the maximum attainable yield of the process while accounting for molecular thermodynamics. In this study, steady-state analysis focused on alkyl levulinate production, the primary target product of alcoholysis. Steady-state was defined as the earliest reaction time at which the alkyl levulinate yield remained constant within experimental uncertainty ($\pm 10\%$) across three consecutive timepoints, providing an objective and reproducible criterion applicable across all feedstocks and temperatures investigated.

By contrast, dialkyl ether formation did not reach steady-state under any conditions tested. Ether synthesis proceeds via dehydration pathways that also generate water, which

competes with the esterification equilibrium required for levulinate formation. Consequently, increased ether production may reduce levulinate yields while simultaneously consuming the alcohol reactant, which represents approximately 38% of the overall process cost [37]. For these reasons, steady-state evaluation was restricted to alkyl levulinate yields, which provide both a robust experimental benchmark and an economically meaningful measure of process performance. These values were subsequently used as the reference basis for kinetic modelling and parameter fitting, ensuring that the derived models were constrained by experimentally validated equilibrium behaviour.

3.6.2 Activation Energies

The kinetic phase experimental data were used to calculate the apparent activation energies of the global butanolysis reactions (Equations 19-22) involved in the formation of *n*-butyl levulinate and di-*n*-butyl ether. Comparable kinetic fittings were performed for ethanolysis by O'Shea et al. [124], but these are not included in this thesis:



The natural logarithm applied to the Arrhenius equation was considered to determine the apparent activation energy for each reaction from the linear fit of $\ln k$ vs. T^{-1} :

$$\ln k = \ln A - \frac{E_A}{RT} \quad (23)$$

where the slope corresponds to $\frac{E_A}{RT}$. The activation energies, E_A , were obtained at 170, 190, and 210 °C.

The activation energies obtained from the calculations were incorporated into the model and fixed as the corresponding parameters for each reaction equation.

3.7 Hierarchical Surrogate Biochemical Kinetic Model for Biomass Alcoholysis

3.7.1 Hierarchical Molecular Group Additivity

A surrogate kinetic model was developed for the sulphuric acid-catalysed alcoholysis of lignocellulosic biomass to provide a hierarchical, molecularly consistent description of reaction pathways and kinetics. The hierarchical mechanism and modelling concept were adapted from previous ethanolysis studies [44, 124], in which a similar progression from simple to complex substrates was shown to be both chemically valid and computationally robust. The surrogate kinetic model utilises a hierarchical learning framework grounded in molecular group additivity, as shown in Figure 20.

The approach is based on the fact that the fundamental monosaccharide structure is conserved across all biomass types. Acid-catalysed cleavage of glycosidic bonds proceeds through the same mechanistic steps for glucose units in solution, in cellulose chains, and in hemicellulose polymers: protonation of the glycosidic oxygen, cleavage to form an oxocarbenium ion, and nucleophilic attack by water or alcohol [183]. This conservation of mechanism allows kinetic parameters determined for glucose to be directly applied to cellulose and subsequently extended to compositionally heterogeneous lignocellulosic feedstocks.

The hierarchy is both chemical and computational. Chemically, the model progresses from simple, chemically well-defined substrates to more compositionally complex materials. For the cellulose pathway, this progression is glucose $\rightarrow$ cellulose $\rightarrow$ real-world lignocellulosic biomass. In parallel, the hemicellulose pathway progresses from xylan $\rightarrow$ real-world lignocellulosic biomass. Computationally, each stage is represented by an independently parameterised sub-model. Kinetic parameters obtained from glucose experiments remain fixed when calibrating the cellulose sub-model; similarly, parameters for glucose and cellulose remain fixed when calibrating the xylan sub-model. This structured

approach maintains chemical self-consistency while avoiding overfitting as model complexity increases.

This hierarchical structure ensures that well-defined sub-models form the foundation for more complex representations, providing a chemically justified and computationally stable framework for modelling biomass alcoholysis kinetics [44, 124].

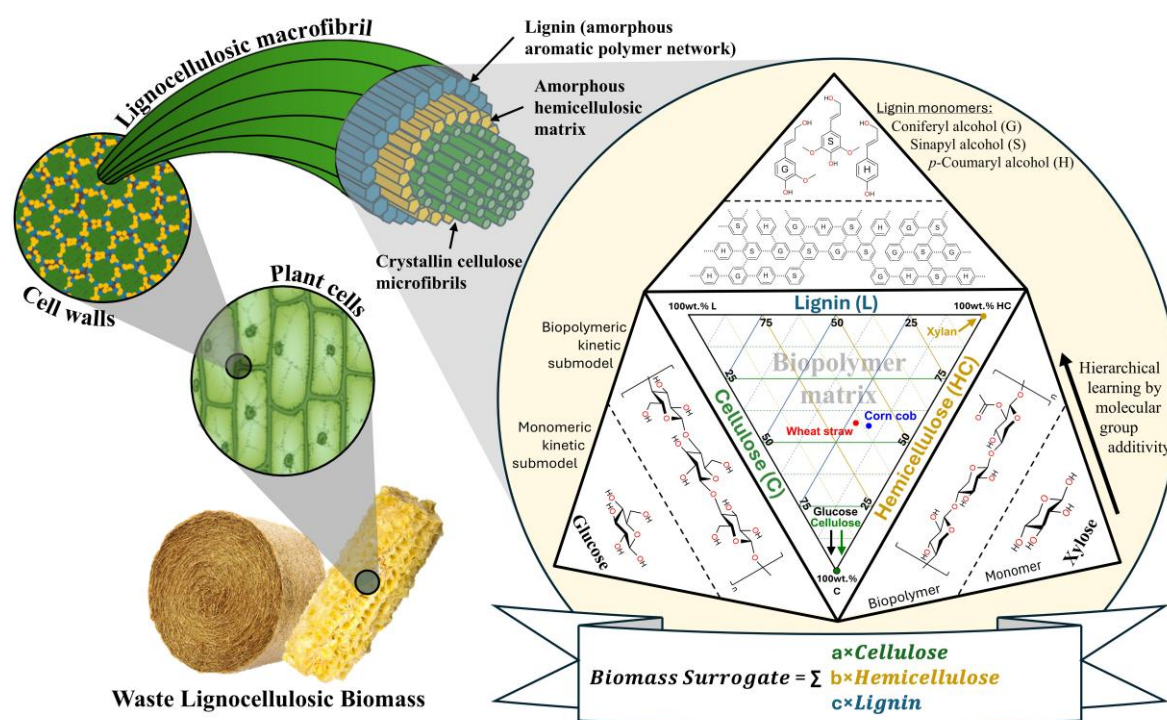


Figure 20. Hierarchical structure and surrogate composition of lignocellulosic biomass, from plant cells to macrofibrils and microfibrils, accompanied by a ternary diagram showing the cellulose, hemicellulose, and lignin contents of various feedstocks, together with representative structural monomers. This schematic forms the basis for the biochemical surrogate hierarchical reaction mechanistic kinetic model.

3.7.2 Biochemical Surrogate Compositional Model

The biochemical surrogate compositional model provides a simplified yet chemically rigorous representation of lignocellulosic biomass, enabling its kinetic behaviour to be modelled in a way that is both mechanistically meaningful and computationally tractable. As illustrated in Figure 20 and detailed in Figure 21, the surrogate concept decomposes the complex architecture of biomass into chemically discrete fractions with distinct reactivities: a carbohydrate fraction, comprising cellulose and hemicellulose, and a non-carbohydrate

fraction, referred to here as remaining mass (containing lignin, extractives, ash and unknowns).

In the kinetic framework, the carbohydrate fraction represents polysaccharides that hydrolyse to monosaccharides and subsequently form liquid products, such as alkyl levulinates. The remaining mass fraction aggregates lignin, extractives, ash, and other uncharacterised non-carbohydrate material. Lignin monomers are not included as kinetic surrogates because, under the studied alcoholysis conditions, they do not measurably contribute to liquid product formation. Instead, this fraction is modelled exclusively as a precursor to humins and soluble unknowns.

The surrogate composition for a given biomass is expressed as:

$$\text{Biomass surrogate composition} = \Sigma X \times \text{Cellulose}, Y \times \text{hemicellulose}, Z \times \text{Remaining mass} \quad (24)$$

Where X, Y and Z are the mass fractions of each constituent. This formulation serves two key purposes:

1. It bridges the compositional complexity of real lignocelluloses with the well-defined chemistry of mono- and polysaccharides used in sub-models.
2. It allows for hierarchical additive learning of reaction kinetics, enabling knowledge gained from chemically simple surrogates to be transferred to more compositionally heterogeneous feedstocks.

Corn cob is modelled to decompose instantaneously into cellulose, hemicellulose (assumed entirely as xylan [184]), and remaining mass, in a ratio of 1.1:1.0:1.6 by weight, based on biochemical composition data in Chapter 4 (Figure 21). Cellulose and hemicellulose are represented as repeating units of anhydrous glucopyranose ($\text{C}_6\text{H}_{10}\text{O}_5$)_n and anhydrous xylopyranose ($\text{C}_5\text{H}_8\text{O}_4$)_n [185], respectively. The composition of the remaining mass is inferred from the residual elemental balance once carbohydrates are accounted for.

The surrogate framework incorporates four sub-models, each justified by its distinct chemistry:

- *Glucose sub-model* – Adapted from the analogous ethanolysis system [51, 61], where glucose is rapidly converted to alkyl glucosides and subsequently to alkyl levulinates

via acid-catalysed pathways, with negligible furanic by-product formation (Figure 23 and 27)

- *Cellulose sub-model* – Captures depolymerisation through both acid butanolysis and acid hydrolysis, reflecting the presence of *n*-butanol and water in the reaction medium.
- *Hemicellulose sub-model (xylan)* – Xylan is selected as a universal hemicellulose surrogate due to its prevalence in terrestrial biomass and its representative chemical structure [184]. Xylan contribution to levulinate formation was discovered upon completing the ethanolysis study and is thus only incorporate in the subsequent butanolysis work. The sub-model accounts for hemicellulose-specific reactions, including deacetylation, pentose release, and furfural formation, which are not captured by cellulose kinetics alone. The contribution of hemicellulose to levulinate formation was first identified through the ethanolysis analysis and is therefore incorporated only in the subsequent butanolysis mechanism (Figure 28).
- *Remaining mass sub-model* – Represents the non-carbohydrate fraction of biomass, modelled exclusively with catalytic and non-catalytic pathways leading to humins and soluble unknowns, thereby capturing acid consumption and phenolic condensation–crosslinking reactions characteristic of lignin-rich feedstocks (Figure 21)

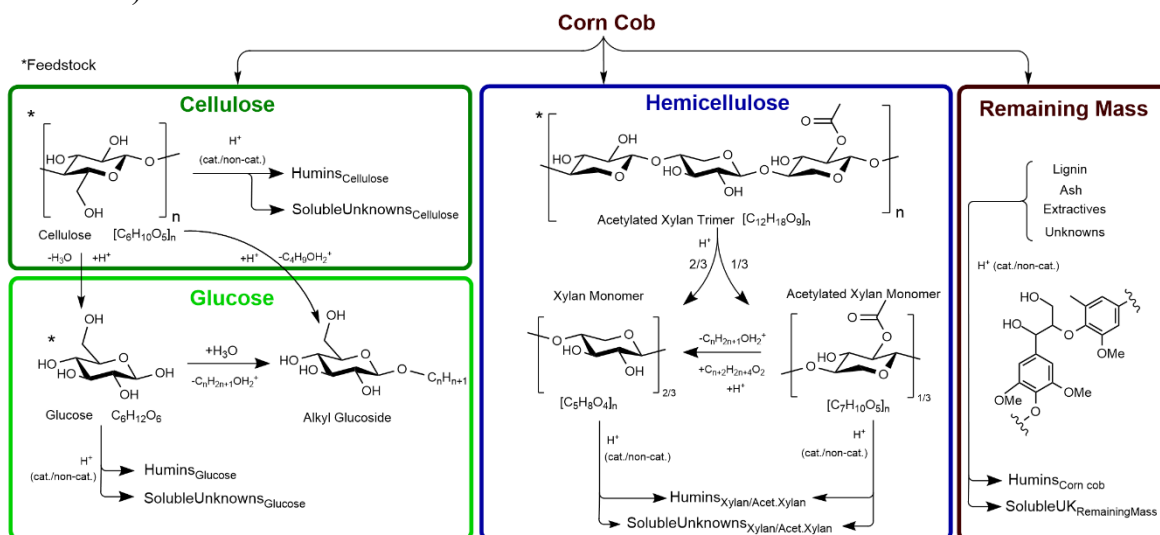


Figure 21. Sub-model outlining the decomposition of corn cob fractions into cellulose, hemicellulose, and remaining mass (lignin, ash, extractives and unknowns). Lignin-derived structures and ash components are shown to contribute to humin formation and soluble unknowns, providing a mechanistic link between whole-biomass composition and observed product distributions.

By explicitly defining the surrogate composition and independently parameterising each fraction's kinetics, this approach reduces parameter uncertainty, preserves chemical self-consistency across the hierarchy, and improves predictive capability when extrapolating from model substrates to diverse lignocellulosic feedstocks. This surrogate-based design also ensures computational stability by fixing parameters determined for simpler surrogates before introducing additional compositional and mechanistic complexity.

3.7.3 Mechanisms of Product Formation

3.7.3.1 Ethanolysis Surrogate Kinetic Model

Reaction conditions of the ethanolysis system

The mechanisms of product formation in the ethanolysis system were developed first and are thus less detailed than the subsequent butanolysis system that was studied. The full mechanism is detailed in Figure 32 in Chapter 5 (Ethanolysis), with the associated reaction set and optimised rate constants listed in Table 14.

A hierarchical surrogate kinetic framework was developed to describe the acid-catalysed ethanolysis of glucose, cellulose, and corn cob at 150 °C with 0.5–2 wt.% sulphuric acid and 5–20 wt.% feedstock. The model incorporates mass-conserved reactions representing the conversion of carbohydrates to ethyl levulinate, as well as competing pathways leading to diethyl ether, humins, and other soluble intermediates.

A key feature of surrogate kinetic model for ethanolysis is the explicit inclusion of diethyl ether formation through ethanol dehydration, an unavoidable side reaction that consumes the valuable solvent. The modelling framework was constructed hierarchically: submodels for glucose were first parameterised, extended to cellulose via depolymerisation pathways, and then generalised to corn cob using a surrogate composition of cellulose, hemicellulose, and lignin fractions derived from biochemical analysis. Protonation and deprotonation steps were incorporated throughout to account for catalytic cycles and proton balance.

The surrogate approach ensured consistency between mechanistic representation and elemental mass conservation, while allowing systematic extension from model compounds

to complex lignocellulosic biomass. This framework provided the basis for subsequent evaluation of ethanolysis kinetics and product distribution.

Diethyl ether



The oversight of diethyl ether as a significant co-product in literature studies of the ethanolysis process is a major shortcoming of previous kinetic models. This gap in understanding contributes to the present limitation in performing an accurate techno-economic-analysis of ethyl levulinate production. In this study, the condensation reaction of ethanol to diethyl ether is represented as an acid-catalysed, reversible reaction (Equation 25). This submodel also includes the protonation and deprotonation of ethanol and water as shown in Figure 22.

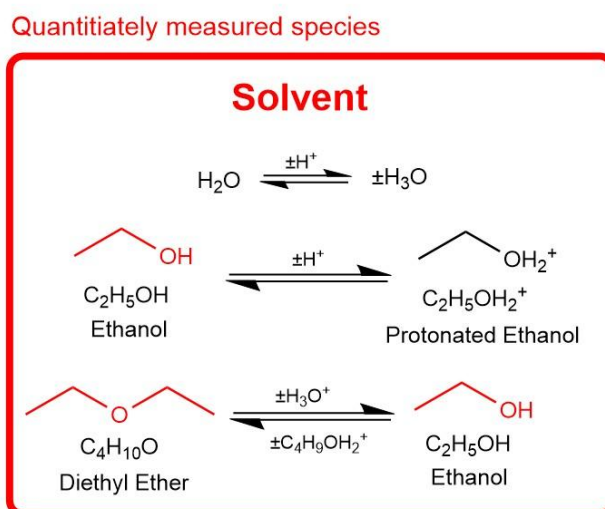
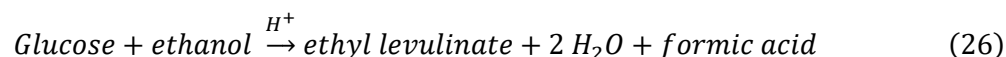


Figure 22. solvent species in the ethanolysis system, showing equilibria between water, ethanol, and diethyl ether with their protonated intermediates under acidic conditions.

Glucose



The conversion of monosaccharide glucopyranose to ethyl levulinate is modelled to proceed through the intermediate ethyl glucopyranoside as shown in Figure 23. This is the main experimentally observed pathway [51]. Humins resulting from glucose ethanolysis is modelled via the formation of “unknowns” from both glucopyranose and ethyl glucopyranoside.

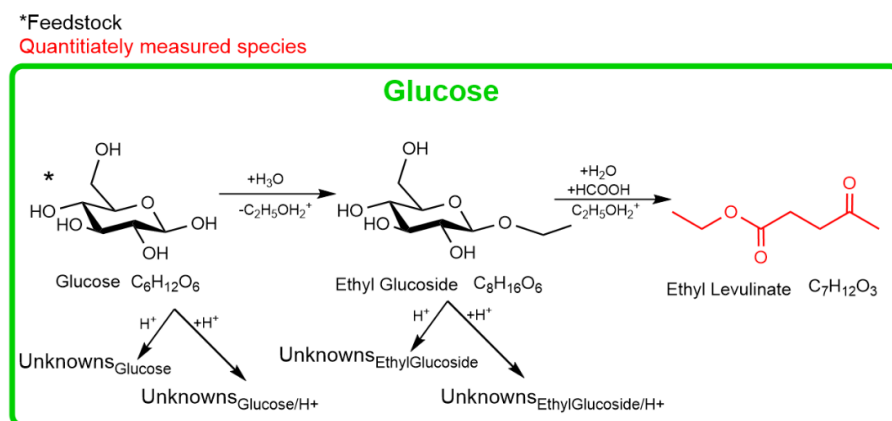


Figure 23. Sub-model representing glucose conversion in ethanolysis. Glucose reacts with ethanol to form ethyl glucoside, which subsequently decomposes to ethyl levulinate, with concurrent formation of formic acid. Parallel routes generate soluble and insoluble unknowns, accounting for humins and other by-products. This pathway highlights the central role of glucose in driving levulinate formation.

Cellulose

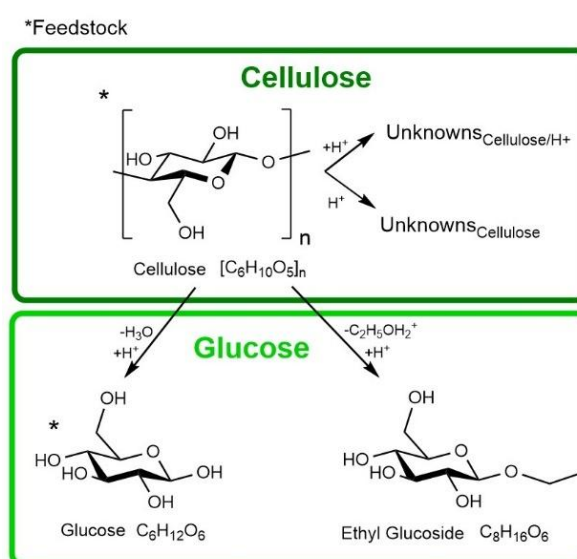


Figure 24. Feedstock pathways in the ethanolysis system, where cellulose depolymerises via acid hydrolysis to form glucose or via acid ethanolysis to yield ethyl glucoside, with humin formation represented by ‘unknown’ intermediates.

The more complex cellulose molecule is modelled to depolymerise via two reaction pathways due to the presence of both ethanol and water in the reaction system: (i) an acid *hydrolysis* pathway and (ii) an acid *ethanolysis* pathway. Cellulose is either depolymerised along the acid hydrolysis pathway to form glucopyranose or throughout the acid ethanolysis pathway to produce ethyl glucopyranoside. Humin formation from cellulose ethanolysis is modelled through the production of “unknowns” (Figure 24). The global reaction to ethyl levulinate is shown in Equation 27.

Corn cob

Corn cob is a representative real-world lignocellulosic biomass. Modelling the chemical reactions of such materials requires addressing the challenge posed by their complex and variable chemical composition. To resolve this, a surrogate approach is proposed. In this framework, the biomass is represented as a synthetic mixture of its principal biopolymers, cellulose, hemicellulose, and lignin, in proportions that reflect the biochemical composition of the actual feedstock. For corn cob, the measured mass fractions are 40.8% cellulose, 46.7% hemicellulose, and 12.5% lignin [54].

In the absence of more detailed structural information, lignocellulose is assumed to depolymerise instantaneously into these three fractions according to the measured ratios (Figure 25). The molecular compositions of cellulose and hemicellulose are defined in terms of their dehydrated monomeric repeating units, $(C_6H_{10}O_5)_n$ and $(C_5H_8O_4)_n$, respectively, corresponding to glucose and xylose [186, 187]. A standardised unit of corn cob is then defined through stoichiometric analysis, such that it decomposes into one mole of cellulose and 0.882 moles of hemicellulose. The lignin contribution is not measured directly but is instead inferred from the residual elemental balance of the biomass.

Ultimate analysis of corn cob indicates the following composition (wt%): carbon 45.0, hydrogen 6.5, oxygen 47.3, nitrogen 1.1, sulphur 0.1, corresponding to an H/C molar ratio of 1.72. By subtracting the known contributions of cellulose and hemicellulose from these totals, the elemental composition of lignin can be determined. This yields an estimated lignin composition of approximately C 45%, H 9%, O 38%, and N+S 10% (on a weight basis), which is consistent with reported values for agricultural residue lignins [188].

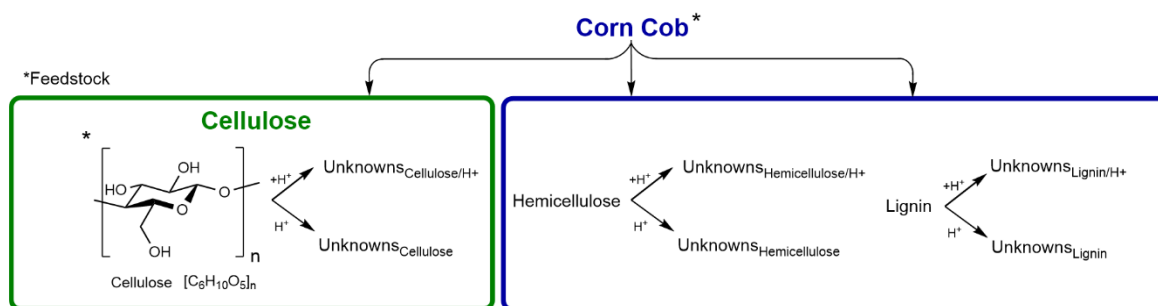


Figure 25. Sub-model outlining the decomposition of corn cob into cellulose, hemicellulose, and lignin fractions. Each fraction generates unknown products through acid-catalysed and non-catalysed reactions. These unknowns represent soluble and insoluble species of unidentified composition, including humins and other condensed residues, linking feedstock complexity to observed product balances.

“Unknowns”

Both non-catalytic and catalytic pathways are modelled to produce “unknowns” from each intermediate, which are essential to describe the partial consumption of the acid. They represent both the formation of humins and other soluble species (humins and soluble unknowns are grouped for ethanolysis work but are separated in subsequent butanolysis studies). The elemental compositions of humins were determined experimentally to have an approximate carbon to hydrogen molar ratio of 1:1. Consequently, this ratio is used as the molecular composition of “unknowns” in the model. Furthermore, it is assumed that “unknowns” formed from lignin maintain a consistent molar ratio to the initial structure and this process yields between 0 and 4.5 water molecules and is detailed in the reactions listed in Table 14 in Chapter 5. The oxygen content of each “unknown” species is inferred from arithmetic involving its precursor intermediate and the number of water molecules produced.

3.7.3.2 Butanolysis Surrogate Kinetic Model

Reaction conditions of the butanolysis system

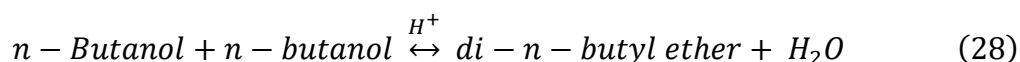
The mechanisms of product formation for the acid catalysed butanolysis of lignocellulosic biomass are summarised in Figure 50 and the associated reaction set and rate constants are listed in Table 19 in Chapter 6 (Butanolysis). The hierarchical biochemical surrogate kinetic model reproduced the concentration–time profiles of the eight most abundant liquid products with high accuracy, confirming its capability to capture the

dominant pathways and kinetics of the butanolysis network. Under the conditions studied, the butanolysis system exhibited reaction pathways, intermediate formation, and kinetic trends analogous to those previously reported for ethanolysis [44, 124], consistent with the shared acid-catalysed cleavage and rearrangement steps.

A notable operational difference was observed in mixture viscosity. While ethanolysis tolerates lignocellulosic biomass loadings of up to 20 wt.% without impairing analysis [44, 124], preliminary butanolysis trials at the same loading produced a highly viscous product mixture unsuitable for reliable gas chromatography quantification. All subsequent experiments were therefore performed at 10 wt.% feedstock loading to ensure analytical accuracy. This higher viscosity is likely related to polymerisation reactions, potentially promoted by furfural concentrations observed in butanolysis, although confirming this effect lies beyond the scope of the present study.

n-Butanol and di-*n*-butyl ether

In the surrogate kinetic model, *n*-butanol is both the solvent and a reactant, with its behaviour modelled following the ethanolysis framework but adapted for the distinct chemical environment of *n*-butanol. The model incorporates the reversible, acid-catalysed etherification of *n*-butanol to di-*n*-butyl ether, represented as:



This step is modelled alongside the protonation and deprotonation equilibria of *n*-butanol and water (Figure 26) informed by density functional theory calculations for ethanol by Howard et. al. [51]. Sulphuric acid is assumed to fully dissociate in *n*-butanol, providing two protons (H⁺) to catalyse both etherification and saccharide conversion pathways. Inclusion of this competitive pathway is essential, as ether formation consumes *n*-butanol that would otherwise participate in the formation of *n*-butyl levulinate.

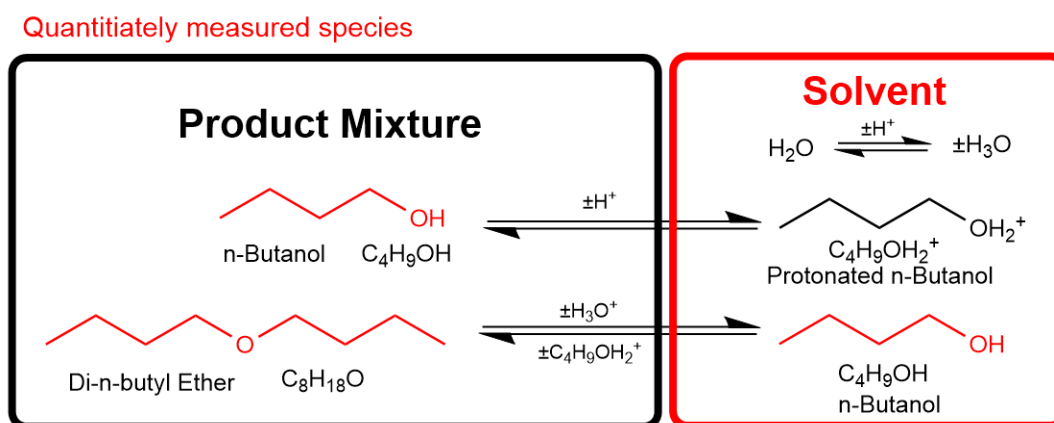


Figure 26. Sub-model illustrating the role of the solvent phase in butanolysis. Protonated *n*-butanol and di-*n*-butyl ether are formed under acidic conditions, alongside reversible hydration of water. These species, often neglected in the literature, were explicitly quantified in this work as key contributors to the three-component advanced biofuel blends produced by alcoholysis.

By incorporating the etherification and protonation equilibria directly into the surrogate kinetic model, the *n*-butanol reaction network is represented in a way that is consistent with the hierarchical framework established for ethanolysis. This ensures that the competitive consumption of *n*-butanol through ether formation, as well as its role in saccharide conversion to *n*-butyl levulinate, is captured without altering the underlying structure of the model. In this way, the butanolysis adaptation preserves mechanistic consistency with ethanolysis while accurately reflecting the distinct reactivity of *n*-butanol.

n-Butyl levulinate

n-Butyl levulinate formation is modelled in both the glucose and hemicellulose (xylan) submodels of the surrogate kinetic framework (Figure 27 and 28). Insights from ethanolysis studies [124] show that glucose is first converted to ethyl glucoside, which then undergoes acid-catalysed rearrangement and hydration to form ethyl levulinate. In the butanolysis model, a similar acid-catalysed pathway is assumed for glucose, proceeding via *n*-butyl glucoside, and for cellulose through sequential depolymerisation to glucose followed by *n*-butyl levulinate formation.

For xylan, direct mechanistic data on the pathway to n-butyl levulinate are limited. To represent this transformation within the surrogate framework, a lumped global reaction is therefore employed. This reaction is constructed to be stoichiometrically balanced, mass-conserving, and chemically analogous to cellulose conversion, but adjusted for the C₅ sugar composition of xylan. In doing so, it captures the essential net chemistry of xylan-derived levulinate formation while avoiding unsupported mechanistic assumptions. The three global reactions are:



This approach ensures that the model remains both mechanistically plausible and quantitatively robust in the absence of detailed kinetic data. Moreover, it provides a practical basis for integrating hemicellulose contributions into the surrogate framework, a critical advance given that these contributions were previously overlooked. Ongoing quantum chemical calculations are expected to refine the exact stoichiometry and mechanistic pathway of this reaction, but until those results are available, the simplified representation adopted here is the most appropriate for capturing the role of xylan in levulinate production.

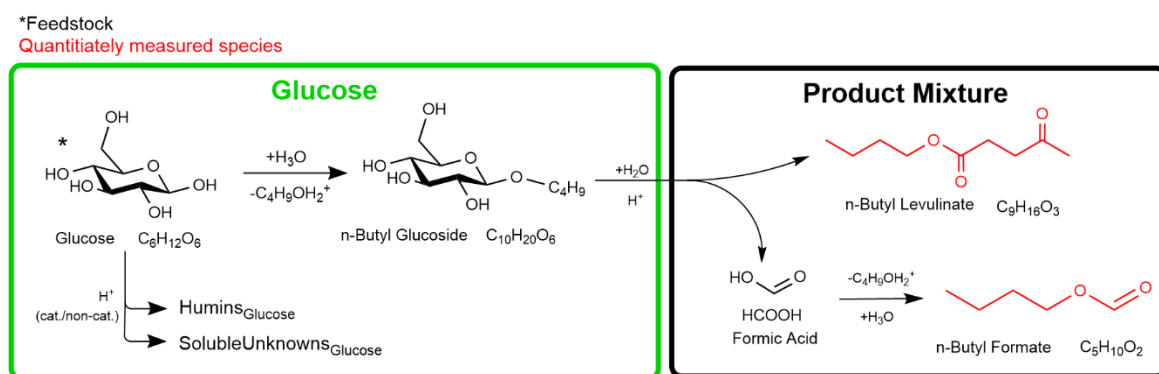
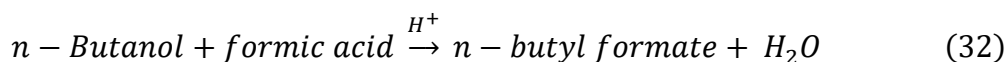


Figure 27. Sub-model representing glucose conversion during butanolysis. Glucose reacts with n-butanol to form n-butyl glucoside, which further transforms into levulinates and formates, with humins and soluble unknowns formed in parallel. This pathway highlights the primary role of cellulose-derived glucose in contributing to alkyl levulinate formation.

n-Butyl formate

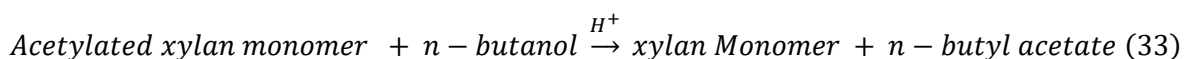
During acid-catalysed butanolysis, *n*-butyl levulinate formation from both cellulose and hemicellulose generates water and formic acid as by-products. Within the surrogate kinetic model, formic acid is further consumed via esterification with *n*-butanol to yield *n*-butyl formate and water:



This pathway is supported by the well-established acid-catalysed esterification of carboxylic acids with alcohols, with analogous formation of ethyl formate from ethanol and formic acid reported under similar conditions [189]. The reaction is expected to proceed efficiently in the butanol-rich medium, consistent with the experimentally observed *n*-butyl formate concentrations. Incorporating this step improves the mass balance for formic acid in the reaction network and enhances the model's ability to capture secondary product formation, thereby increasing predictive accuracy and providing a mechanistic basis for future process optimisation.

n-Butyl acetate

Acid-catalysed butanolysis of acetylated hemicellulose produces *n*-butyl acetate via cleavage of acetyl substituents and subsequent esterification with *n*-butanol:



Significant formation of *n*-butyl acetate was observed for xylan and corn cob, reaching up to 41 wt.% relative to *n*-butyl levulinate, whereas glucose and cellulose yielded only trace amounts. A control experiment using xylopyranose, which lacks acetyl groups, produced negligible *n*-butyl acetate, confirming its origin in acetyl substituents of hemicellulosic fractions.

¹H NMR spectroscopy measurements of the isolated xylan from corn core revealed a monomer-based degree of acetylation of 0.34. This corresponds to approximately one acetyl group per three anhydrous xylopyranose units, assuming no other substituents are present. Similar quantities of *n*-butyl acetate were observed in reactions with both isolated xylan and

corn cob, implying either a higher degree of acetylation in the native xylan within corn cob or the presence of additional acetylated species in the biomass matrix, such as lignin.

The proposed reaction mechanism involves the acid-catalysed cleavage of acetyl groups from the xylan backbone, which then react with protonated *n*-butanol to yield *n*-butyl acetate and regenerate H^+ . This esterification pathway is analogous to mechanisms proposed in hydrolysis systems for acetic acid and aligns with observed reaction behaviour in butanolysis systems [63, 126, 178, 190, 191].

Following deacetylation, the liberated xylopyranose monomer may undergo further transformation to products such as *n*-butyl levulinate or furfural and contribute to humin formation [192, 193]. Incorporation of this acetyl-driven esterification mechanism into kinetic models significantly improves their predictive capability concerning product distributions and better reflects the underlying chemistry of lignocellulosic butanolysis.

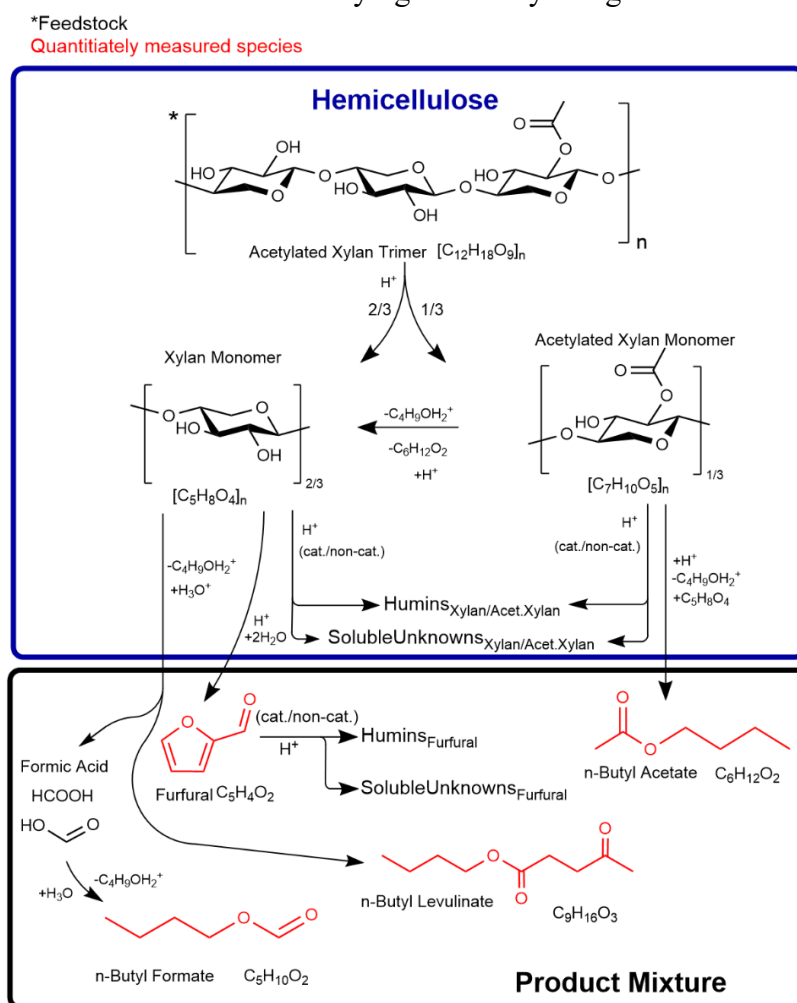
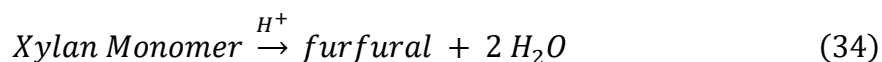


Figure 28. Sub-model illustrating hemicellulose conversion pathways. Xylan-derived monomers and acetylated xylan units yield levulinates, formates, furfural, and acetates, alongside humins and soluble unknowns. This analysis demonstrates that hemicellulose contributes significantly to alkyl levulinate formation, broadening the recognised feedstock base for alcoholysis beyond cellulose alone.

Furfural

Furfural was detected as a transient intermediate in the butanolysis of xylan and corn cob but was absent in glucose and cellulose reactions. This is consistent with its formation via acid-catalysed dehydration of xylose, the principal hemicellulosic sugar released during xylan depolymerisation, as previously reported [178, 194, 195].



This pathway, adapted from established hydrolysis chemistry, has been incorporated into the kinetic model, extending earlier ethanolysis-based frameworks [44, 124]. Although furfural is not proposed as an intermediate in *n*-butyl levulinate formation, it is a key precursor to humins. To investigate this role, furfural (10 wt.%) was subjected to butanolysis conditions (1 wt.% H₂SO₄, reaction times and temperatures as herein) and yielded predominantly insoluble solids with negligible supernatant, indicating its rapid polymerisation under acidic, butanol-rich conditions. While the detailed mechanistic contribution of furfural to humin formation remains outside the scope of this study, its explicit inclusion in the reaction network is essential for accurate kinetic modelling and for guiding future strategies to suppress humin formation.

Water

In the acid-catalysed butanolysis of lignocellulosic biomass, water is generated as a stoichiometric by-product of key transformation steps, including carbohydrate esterification to *n*-butyl levulinate and etherification of *n*-butanol. Within the surrogate kinetic model, water production is determined directly from the balanced reaction scheme [44, 124], ensuring internal mass conservation across all sub-models. Accurate quantification of water is essential, as it influences reaction equilibria, proton activity, and potential hydrolysis side reactions. The validity of this stoichiometric treatment is supported by near-complete mass closure in glucose butanolysis experiments, where over 99 % of the initial carbon mass was accounted for in measured products and humins. Incorporating water explicitly into the hierarchical reaction mechanism ensures mechanistic fidelity and strengthens predictive capability for process optimisation.

Humins

Humins, defined here as the insoluble solid residues generated during acid-catalysed butanolysis, are quantified experimentally by centrifuging the reaction mixture, recovering the solids, and drying them to constant mass. Elemental composition (CHNOS) is subsequently determined via elemental analysis, and the resulting data are incorporated into the surrogate kinetic model to ensure accurate elemental mass closure.

Humins are formed through complex polymerisation and condensation reactions, primarily involving dehydration products of carbohydrates such as 5-hydroxymethylfurfural (HMF) and furfural, along with phenolic fragments derived from lignin-rich fractions [196, 197]. In the butanolysis system, the “remaining mass” sub-model captures these transformations, with humin formation modelled as the sole fate of non-carbohydrate solids, in addition to contributions from carbohydrate-derived intermediates. Although humins are traditionally regarded as an undesirable sink of carbon that reduces liquid fuel yields, emerging studies highlight their potential applications in materials, carbon sequestration, and soil amendment [131].

Including humins explicitly in the reaction network is therefore essential, both to accurately represent carbon flows within the system and to inform process design strategies that either minimise their formation to maximise fuel yields or valorise them as co-products in an integrated biorefinery context.

Soluble unknowns

For corn cob butanolysis, overall mass balances closed to approximately 92%, indicating that a fraction of the reaction products was not directly identified. To maintain mass conservation in the kinetic model, these unquantified soluble species were grouped into a composite category termed “soluble unknowns.” Prior to analysis, all solid residues were removed by centrifugation and weighed, ensuring that the remaining unaccounted mass could be attributed exclusively to dissolved, unidentified products in the liquid phase.

In the reaction network, soluble unknowns are generated via mass-conservation pathways from multiple sources, including the degradation of cellulose, glucose, xylan,

acetylated xylan, furfural, and residual biomass. While this fraction is likely composed of a diverse range of low-concentration intermediates and secondary products, its overall contribution to the total product spectrum remains small, as all major liquid and solid products have been explicitly quantified. Nevertheless, calculating the inferred elemental composition of soluble unknowns offers valuable clues to their molecular characteristics, possible formation pathways, and roles within the reaction network. Incorporating this fraction into the surrogate kinetic model not only enforces elemental mass closure but also ensures that minor species contributions are reflected in process-scale yield predictions.

3.7.4 Kinetic modelling and optimisation

The kinetic modelling in this work utilises Cantera [60], an open-source mathematical solver for problems involving chemical kinetics and thermodynamics. A homogeneous 0-D reactor model is used, where all state variables are functions of time and thermodynamic equilibrium. The initial thermodynamic and chemical state is defined by declaration of pressure, temperature, and species mass fraction with the ideal gas equation of state employed.

The heating and isothermal phases of the reactor are modelled using a reactor network consisting of a reactor interconnected through a heat-conducting wall with an external reservoir at the given reaction. At $t = 0$, the reactor is at 25 °C. The heat flux, q , through the wall is computed by $q = U(T_{reactor} - T_{reservoir})$, where U is the heat transfer coefficient, and $T_{reactor}$ and $T_{reservoir}$ are the temperature of the reactor and reservoir, respectively. U is optimised so that the temperature profile of the model reactor maps its experimental temperature profile in the aluminium block.

A set of ordinary differential equations is numerically solved using Cantera to describe the concentrations of the species in the system as a function of time. An exemplar differential conversion equation for glucose in ethanolysis reaction is given by Equation 35:

$$\frac{d[glucose]}{dt} = k_8[H_3O^+][cellulose] - (k_4)[C_2H_5OH_2^+][glucose] - (k_6)[H^+][glucose] \quad (35)$$

where k_8 is the rate constant for the production of glucose from cellulose, and k_4 and k_6 are the rate constants for the conversion of glucose to ethyl glucoside and “unknown_{SGlucose}”,

respectively. All reactions progress according to their rate constant, k , with Arrhenius temperature dependence as shown in Equation 36:

$$k = Ae^{\left(\frac{-E_A}{RT}\right)} \quad (36)$$

Each k is defined by an activation energy (E_A) and a pre-exponential coefficient (A). Each E_A and A are determined by a hierarchical, sub-model by sub-model optimisation procedure, where computed time resolved species fractions are compared to the time-resolved species fractions observed in experiments.

The optimisation procedure was performed using Phase 1 of the in-house developed Machine Learned Optimisation of Chemical Kinetics (MLOCK) framework [55]. Although MLOCK is designed as a broader optimisation platform, only its initial phase is employed in this work. This phase does not constitute machine learning in the conventional data-driven sense but instead performs a stochastic exploration of kinetic parameter space within physically constrained bounds.

Phase 1 of MLOCK generates a large population of candidate kinetic models, approximately 80,000 in this study, by randomly assigning Arrhenius parameters, E_A and A for each reaction step within predefined physically meaningful ranges. Pre-exponential factors are sampled up to the diffusion limit of $1 \times 10^{-13} \text{ cm}^3 \text{ mol}^{-1}$. This procedure functions as a parameter seeding and screening step, analogous to the initial population generation stage of a genetic optimisation algorithm, rather than as an adaptive learning process.

Each candidate model is evaluated under all experimental conditions for which time-resolved data are available. Model performance is quantified using a least-squares error function that captures the deviation between experimentally observed and model-predicted species masses, averaged across all experimental conditions:

$$Error_i = \sum_{All \text{ exp conditions}} \frac{\sum_{t=0}^{t_f} \left(\frac{x_{exp,i}^t + x_{model,i}^t}{x_{exp}^t} \right)^2}{N_{exp}} \quad (37)$$

where $x_{exp,i}^t$ is the mass of species i measured experimentally after time t , $x_{model,i}^t$ is the mass of species i calculated by the model after time t and, N_{exp} is the number of experimental data points at that condition. The errors observed are used to set narrower

ranges of E_A and A for each reaction through a bound refinement algorithm. A second library of 80,000 model candidates is generated at these refined ranges. A genetic seed scan is then performed centred on the resulting model candidate with the lowest error. The model candidate exhibiting the lower error function after these three iterations of optimisation is deemed to be the optimised model, and the corresponding rate constants are selected as the empirical rate constants, which allows for the best reproduction of the experimental data.

Each sub-model in Figure 32 for ethanolysis and Figure 50 for butanolysis, is optimised individually in hierarchical order to the corresponding experimental data based on the molecular complexity of the feedstock. Once derived, the rate constants for each sub-model are fixed in the overall system during subsequent optimisations.

3.7.5 Model Limitations and Scope

The kinetic modelling framework developed in this work is intended to support mechanistic interpretation of alcoholysis systems and to rationalise experimental trends, rather than to serve as a fully predictive description of industrial reactor performance. Within this defined objective, several limitations should be explicitly acknowledged.

The reaction networks employed represent simplified descriptions of chemically complex systems. Only reaction pathways that are experimentally observed, strongly supported by literature, or required to reproduce dominant product formation trends are included. Minor intermediates and secondary degradation pathways are therefore not explicitly resolved. This level of simplification is appropriate for capturing global behaviour, such as product selectivity and time dependent conversion, while avoiding unnecessary complexity that cannot be robustly parameterised using the available experimental data.

Parameter non uniqueness is an inherent limitation of kinetic modelling in highly coupled reaction networks, particularly where lumped species are employed. Multiple combinations of Arrhenius parameters can reproduce experimental concentration profiles with comparable accuracy. In this work, this limitation is mitigated by constraining all parameters within physically meaningful bounds and by screening a large population of candidate models. Model selection is based on the ability to reproduce experimentally

observed trends across conditions, rather than on uniqueness of individual kinetic parameters, which are therefore interpreted as effective descriptors of system behaviour.

The treatment of residual mass reflects a deliberate modelling choice rather than incomplete mass balance closure. In the ethanolysis model, all unaccounted soluble and insoluble material is grouped into a single “unknowns” term. In the subsequent butanolysis model, improved mechanistic understanding enabled explicit inclusion of humin formation pathways, allowing the residual term to be refined to soluble unknowns only. This progression reflects the evolving level of chemical resolution across the thesis and highlights that residual terms represent chemically meaningful material that is not fully resolved at the current modelling depth.

The models further assume homogeneous reaction conditions, ideal mixing, and uniform temperature profiles, and do not explicitly account for mass transfer limitations, phase behaviour, catalyst deactivation, or reactor hydrodynamics. These effects are expected to become important at larger scales but are outside the scope of the present work, which focuses on intrinsic reaction behaviour under controlled laboratory conditions.

Accordingly, the models are not intended to predict absolute process performance or scale dependent efficiencies. Instead, they provide a consistent and internally coherent framework for interpreting experimental data, identifying dominant reaction pathways, and comparing alcoholysis systems under different conditions. Within this scope, the modelling approach is well suited to the objectives of this thesis, while recognising that further refinement would be required for direct industrial application.

Chapter 4

Feedstock Analysis

4.1 Introduction

Lignocellulosic biomass represents the largest renewable organic carbon resource on earth and is central to the production of advanced biofuels and bio-based chemicals. Its utilisation provides a sustainable route to displace fossil carbon, reduce greenhouse gas emissions, and advance circular economy objectives. However, biomass is inherently heterogeneous, comprising cellulose, hemicellulose, lignin, extractives, and mineral ash in variable proportions depending on species, growth conditions, and processing history [35, 198]. This compositional variability strongly influences reactivity, product yields, and the formation of undesirable by-products.

Cellulose, the most abundant structural polysaccharide, is the dominant precursor of levulinates and related platform molecules, providing the primary source of fermentable hexoses. The work presented in this thesis demonstrates that hemicellulose makes a significant contribution to product formation, particularly through xylan, the principal hemicellulose in hardwoods and herbaceous plants. Importantly, it is shown that acetyl substituents within the xylan structure are cleaved under alcoholysis conditions to form alkyl acetate esters, directly linking hemicellulose chemistry to by-product distributions [124]. Lignin, with its aromatic, cross-linked structure, continues to act as a barrier by reducing carbohydrate accessibility and promoting humin and char formation, while extractives and ash remain inhibitory by limiting catalyst access and neutralising acidic environments [35].

For these reasons, robust compositional analysis is an essential first step in assessing the suitability of biomass for alcoholysis-based biofuel production. Establishing a detailed biochemical and elemental dataset enables:

1. identification of compositional features governing reactivity,
2. comparative evaluation of candidate feedstocks,
3. development and validation of kinetic models, and
4. more reliable techno-economic and life-cycle assessments.

This chapter therefore characterises selected Annex IX feedstocks and model carbohydrates to provide the foundation for subsequent evaluation of reactivity and surrogate-based kinetic modelling. By integrating real feedstocks with surrogates such as glucose, cellulose, and xylan, it is possible to capture the essential biochemical drivers of conversion performance while reducing the need for exhaustive experimental testing.

4.1.1 Regulatory and Sustainability Context

The sustainable deployment of biomass for advanced biofuel production is shaped by regulatory frameworks, most prominently the European Union Renewable Energy Directive. Annex IX of RED II/RED III identifies eligible feedstocks for advanced biofuels, prioritising wastes and residues that avoid competition with food and feed markets. This reflects the dual policy objectives of reducing greenhouse gas emissions from the transport sector while preventing indirect land-use change and safeguarding food security [27].

By restricting this study to Annex IX Part A feedstocks, the experimental scope is aligned directly with EU sustainability policy. This ensures that the findings are both scientifically rigorous and industrially relevant, focusing on materials most likely to support large-scale deployment of advanced biofuels. The emphasis on wastes and residues also enhances environmental and economic value, as these materials are abundant, underutilised, and often pose disposal challenges.

Annex IX encompasses a wide spectrum of biomass categories, including agricultural residues (e.g. straws, husks, nut shells), forestry residues (e.g. thinnings, bark, sawdust), industrial by-products such as bagasse, and non-food energy crops like miscanthus and aquatic biomasses. This diversity mirrors the heterogeneity of European biomass supply

chains and highlights the need for comparative compositional analysis to understand how distinct feedstock classes influence downstream conversion.

4.1.2 Feedstock Selection Criteria

The feedstocks investigated in this study were selected according to three overarching criteria: regulatory compliance, compositional diversity, and practical availability.

Regulatory compliance. Only feedstocks listed in Annex IX Part A of RED II/RED III were included, ensuring alignment with EU sustainability frameworks and policy relevance [27]. This guarantees that the dataset reflects materials prioritised for industrial biofuel deployment and excludes food-competitive crops.

Compositional diversity. To capture the breadth of lignocellulosic resources, the selection represents herbaceous, woody, and aquatic biomass categories, each characterised by distinct balances of cellulose, hemicellulose, lignin, extractives, and ash [198]. In addition, model carbohydrates (glucose, cellulose, xylan) were included as mechanistic surrogates for the primary polysaccharide fractions, providing both experimental control and the foundation for the hierarchical surrogate kinetic modelling framework [124].

Practical availability. Within each Annex IX category, feedstocks were prioritised based on abundance, generation rates, and underutilisation. Agricultural residues such as wheat straw and oat husks are among the most widely available lignocellulosic resources in Europe [199-201], while nut shells, exemplified by peanut shells, are generated at large scale in global processing industries [202, 203]. Forestry residues such as Sitka spruce thinnings are produced extensively during timber operations, particularly in Ireland where Sitka spruce dominates commercial forestry [204]. Dedicated energy crops like *miscanthus* × *giganteus* offer high yields and resilience [205, 206], while aquatic biomasses such as water hyacinth provide the dual benefit of ecological management and renewable fuel production [207].

This strategy ensures that the selected feedstocks are not only policy-compliant but also representative of the compositional and logistical diversity that will shape the industrial deployment of advanced biofuel processes.

4.1.3 Feedstocks Selected

Nine Annex IX Part A feedstocks were chosen to reflect the compositional and logistical diversity of lignocellulosic biomass. These represent agricultural residues, industrial by-products, forestry residues, aquatic biomass, and a dedicated energy crop. In addition, three model carbohydrates (glucose, cellulose, xylan) were included as surrogates for the primary polysaccharide fractions.

Table 6. Selected Biomass Feedstocks and Their Regulatory Classifications.

Biomass	Species	Biomass Type	Supply Sector	Annex IX
Brussels sprout residue	<i>Brassica oleracea gemmifera</i>	Herbaceous & Agricultural	Food industry residue	(d)
Wheat straw	<i>Triticum aestivum</i>	Herbaceous & Agricultural	Agricultural	(e)
Sugarcane bagasse	<i>Saccharum officinarum</i>	Herbaceous & Agricultural	Food industry	(j)
Peanut shells	<i>Arachis hypogaea</i>	Herbaceous & Agricultural	Agricultural	(l)
Oat husks	<i>Avena sativa</i>	Herbaceous & Agricultural	Agricultural	(m)
Beechwood chippings	<i>Fagus sylvatica</i>	Wood & Woody	Forestry & wood industry	(o)
Sitka spruce thinnings	<i>Picea sitchensis</i>	Wood & Woody	Forestry & wood industry	(o)
Water Hyacinth	<i>Pontederia crassipes</i>	Aquatic	Dedicated Energy crops	(p)
Miscanthus	<i>Miscanthus × giganteus</i>	Herbaceous & Agricultural	Dedicated energy crops	(p)

The selected feedstocks span a broad continuum of carbohydrate content, lignin recalcitrance, extractive fractions, and ash levels, allowing systematic evaluation of compositional influences on alcoholysis reactivity:

Agricultural residues

Wheat straw is one of the most abundant residues in Europe, produced at nearly one million tonnes annually in Ireland alone [199, 200]. Oat husks, a by-product of cereal milling, are compositionally rich in cellulose (over 50%) [201]. Brussels sprout residue represent a more novel agricultural waste, abundant but compositionally challenging due to their unusually high extractives (41.6%) and ash (9.9%). Peanut shells, generated at large scale in global processing industries, combine high cellulose with elevated lignin content [202, 203].

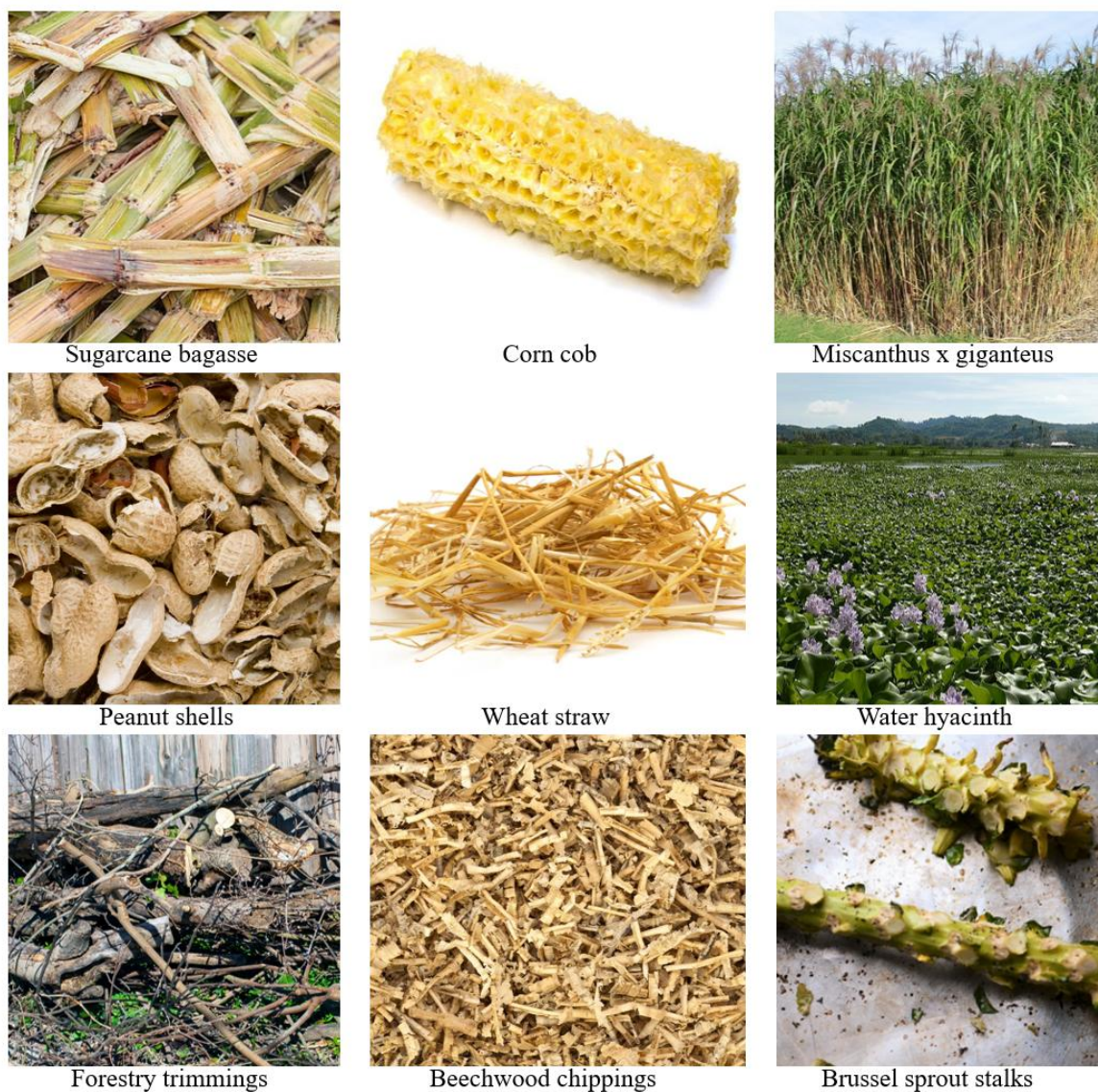


Figure 29. Selected Annex IX feedstocks under the Renewable Energy Directive (RED).

Industrial by-products

Sugarcane bagasse is among the most established feedstocks for advanced biofuels, with high cellulose and hemicellulose fractions and very low ash content [208]. While geographically concentrated in sugar-producing regions such as Brazil and India, it remains a valuable reference point for compositional benchmarking.

Forestry residues

Beechwood chippings (hardwood) and Sitka spruce thinnings (softwood) provide contrasting examples within Annex IX (o). Beechwood offers a relatively balanced composition with low ash, while Sitka spruce exemplifies a highly lignified, high-ash feedstock, reflecting the recalcitrance of softwoods [204]].

Aquatic biomass

Water hyacinth, an invasive aquatic species, was included as a representative non-food, cellulosic aquatic biomass. While it offers ecological mitigation potential and rapid growth rates, its low carbohydrate fraction and exceptionally high ash content (26.8%) present significant processing challenges [207].

Dedicated energy crop

Miscanthus × giganteus combines high yields, favourable cellulose content, and low ash levels with the ability to thrive on marginal land [205, 206]. It represents one of the most scalable biomass options in European contexts.

Collectively, this set of feedstocks ensures that the experimental analysis captures both promising candidates (e.g. oat husks, miscanthus, sugarcane bagasse) and more recalcitrant examples (e.g. Sitka spruce, water hyacinth, Brussels sprout residue). This diversity provides the foundation for evaluating compositional-performance relationships in alcoholysis and validating the surrogate-based kinetic modelling framework.

4.2 Objectives

The objective of this chapter was to establish a compositional framework for evaluating the suitability of RED II/RED III Annex IX lignocellulosic feedstocks and model carbohydrates in alcoholysis-based biofuel production. Specifically, the aims were:

1. To identify promising and compositionally diverse Annex IX feedstocks, capturing agricultural, forestry, aquatic, and industrial residues alongside energy crops, in order to reflect the heterogeneity of real biomass supply chains.
2. To determine elemental composition of selected feedstocks and surrogates, quantifying carbon, hydrogen, nitrogen, sulphur, and oxygen contents, and evaluating their implications for theoretical energy density and potential catalytic inhibition.
3. To quantify biochemical fractions using the NREL protocol, establishing cellulose, hemicellulose, lignin, extractive, and ash contents to differentiate favourable from recalcitrant feedstocks.
4. To incorporate surrogate carbohydrates (glucose, cellulose, and xylan) as benchmarks of increasing structural complexity, linking controlled mechanistic behaviour to whole-biomass reactivity and supporting the development of a hierarchical surrogate kinetic framework.
5. To assess the structural role of hemicellulose acetylation, using quantitative ^1H NMR spectroscopy of xylan to determine the degree of substitution and its influence on alkyl acetate formation under alcoholysis conditions.

By fulfilling these objectives, this chapter provides a comparative dataset that highlights both high-potential feedstocks (oat husks, miscanthus, sugarcane bagasse, wheat straw) and less favourable examples (Sitka spruce, Brussels sprout residue, water hyacinth). The surrogate analysis ensures mechanistic control, while xylan acetylation is directly linked to by-product distributions. Together, these outcomes establish the foundation for the experimental alcoholysis and surrogate-based kinetic modelling developed in the following chapters. Importantly, while the full suite of Annex IX feedstocks has been characterised here, their experimental evaluation under alcoholysis conditions lies beyond the scope of this thesis and will form the basis of subsequent PhD projects.

4.3 Methodologies Employed

The methodologies applied in this chapter followed directly from the analytical procedures detailed in Chapter 3. Elemental composition of all feedstocks was determined by ultimate analysis using an Elementar EL Cube analyser, quantifying carbon, hydrogen,

nitrogen, sulphur, and oxygen contents directly (Section 3.4.2). Biochemical composition, including cellulose, hemicellulose, and lignin fractions, was quantified according to the NREL two-stage acid hydrolysis procedure (Section 3.4.3). The degree of acetylation in hemicellulosic substrates was determined by quantitative ^1H NMR spectroscopy (Section 3.4.4).

Together, these analyses established a consistent and quantitative basis for benchmarking the composition of lignocellulosic feedstocks, enabling accurate normalisation of alcoholysis yields and mechanistic comparisons in the subsequent experimental chapters.

4.4 Results and Discussion

4.4.1 Elemental Analysis of Feedstocks

Elemental composition provides a first indication of the suitability of biomass for alcoholysis, as carbon content, H/C ratios, and heteroatom levels govern both theoretical yields and potential side-reactions.

Across the dataset, a continuum can be observed from simple sugars to highly lignified biomasses. Glucose and xylose exhibit relatively low carbon contents (40 wt%) but high H/C ratios (2.00), reflecting their high reduction state and reactivity. Cellulose (44.4 wt% carbon) and xylan (45.5 wt% carbon) are oxygenated polymers, with lower H/C ratios (1.60–1.66), serving as more realistic surrogates for lignocellulosic material.

Among the Annex IX feedstocks, carbon content spans from 32.4 wt% (water hyacinth) to 47.6 wt% (peanut shells). High-carbon feedstocks such as peanut shells (47.6 wt%) and Sitka spruce (47.1 wt%) illustrate the influence of lignin, which increases carbon density while lowering the H/C ratio. In contrast, low-carbon feedstocks such as water hyacinth (32.4 wt%) and Brussels sprout residue (39.1 wt%) are diluted by elevated nitrogen, sulphur, and ash fractions, reducing their effective energy density.

H/C ratios further differentiate feedstocks: softwoods such as Sitka spruce show the lowest values (1.52), consistent with high lignin recalcitrance, while agricultural residues such as Brussels sprout residue (1.89) and oat husks (1.83) exhibit higher H/C values, closer to reactive polysaccharides.

Chapter 4. Feedstock Analysis

Table 7. Ultimate analysis (wt.%) of dried feedstocks. Elemental composition was determined by CHNS and O analysis.

Ultimate Analysis (wt%)						
	Carbon	Hydrogen	Oxygen	Nitrogen	Sulphur	Molar H/C
Sugars and carbohydrates						
Glucose	40.0	6.7	53.3	0.0	0.0	2.00
Cellulose	44.4	6.2	49.4	0.0	0.0	1.66
Xylan	45.5	6.1	48.5	0.0	0.0	1.60
Xylose	40.0	6.7	53.3	0.0	0.0	2.00
Biomasses						
Brussels Sprout Residue	39.1	6.2	46.2	1.8	0.7	1.89
Corn cob	45.0	6.5	47.3	1.1	0.1	1.72
Wheat Straw	44.5	6.3	45.0	0.4	0.0	1.69
Sugarcane Bagasse	46.1	6.1	46.6	1.0	0.0	1.58
Peanut Shells	47.6	6.2	45.2	1.0	0.2	1.55
Oat Husks	43.6	6.7	46.0	1.4	0.1	1.83
Beechwood Chippings	45.6	6.3	46.8	0.2	0.0	1.65
Sitka Spruce Thinnings	47.1	6.0	38.7	1.2	0.1	1.52
Water Hyacinth	32.4	4.9	36.3	2.1	0.2	1.80
Miscanthus	45.4	6.3	45.7	0.4	0.0	1.65

Nitrogen and sulphur contents are generally low (<1 wt%), though Brussels sprout residue (1.8 wt% nitrogen, 0.7 wt% sulphur) and water hyacinth (2.1 wt% nitrogen, 0.2 wt% sulphur) are exceptions. These heteroatoms may complicate processing by introducing non-carbonaceous by-products or causing catalyst poisoning. By contrast, beechwood and miscanthus display negligible levels, highlighting their suitability as clean feedstocks.

Taken together, elemental analysis shows that:

- Clean, carbon-rich feedstocks (e.g. wheat straw, corn cob, peanut shells, sugarcane bagasse, miscanthus, beechwood) are most promising in terms of energy density and theoretical carbon yield.
- Ash- and heteroatom-rich feedstocks (e.g. Brussels sprout residue, water hyacinth) are compositionally less favourable, likely requiring pre-treatment or catalyst adjustments.
- Surrogate carbohydrates bracket the observed elemental trends, providing a useful baseline for interpreting biomass behaviour.

4.4.2 Biochemical Analysis of RED II/RED III Annex IX Feedstocks

4.4.2.1 Overview of Lignocellulosic Biomass Composition

Lignocellulosic biomass is a heterogeneous matrix of structural carbohydrates, lignin, extractives, and inorganic ash. The relative proportions of these components determine the extent to which a feedstock can be converted into alkyl levulinates and related bio-based intermediates. Cellulose and hemicellulose constitute the principal polysaccharides targeted for depolymerisation and hydrolysis to levulinic acid and its esters, including *n*-butyl levulinate [35, 198]. Among hemicellulosic polysaccharides, xylan is particularly important in hardwoods and herbaceous species due to its acetyl substituents, which can yield additional by-products such as alkyl acetates during alcoholysis [185].

Lignin, by contrast, contributes recalcitrance to biomass conversion. Its aromatic, cross-linked structure forms a barrier to acid penetration and carbohydrate hydrolysis, while lignin-derived phenolics can undergo condensation reactions to form humins or inhibit catalytic pathways [209-212]. Extractives, a diverse group of low-molecular-weight compounds including fats, waxes, phenolics, and soluble sugars, may interfere with catalytic processes by reacting with intermediates or consuming protons, thereby diverting pathways away from levulinate production [213]. Inorganic ash, dominated by alkali and alkaline earth metals, further complicates processing by buffering acidic catalysts, reducing effective proton concentration, and in some cases promoting unwanted side reactions [214].

The selected Annex IX feedstocks encompass a wide range of these biochemical fractions, reflecting their agricultural, forestry, aquatic, and industrial origins. Table 8 presents the full biochemical analysis of all investigated feedstocks, while Figure 30 illustrates these differences visually. Together, they highlight the diversity of composition across residues and energy crops, emphasising the importance of comparing carbohydrate availability, lignin recalcitrance, extractive burden, and ash content when assessing feedstock suitability for alcoholysis.

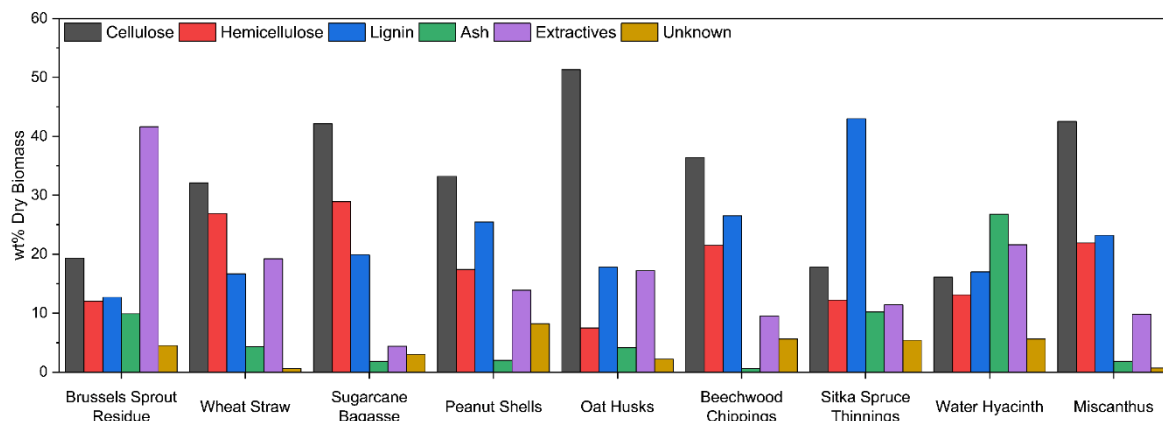


Figure 30. Biochemical composition of the biomasses studied in this investigation measured using NREL procedure for determination of structural carbohydrates and lignin in biomass [215].

4.4.2.2 Carbohydrate Fractions and Conversion Potential

Cellulose and hemicellulose constitute the principal structural carbohydrates in lignocellulosic biomass and are the primary precursors of levulinic acid and its esters in acid-catalysed alcoholysis. The abundance and accessibility of these polysaccharides strongly influence theoretical yields of alkyl levulinates, while compositional differences across feedstocks determine the severity of conditions required for efficient conversion [35, 198].

As shown in Table 8 and Figure 30, carbohydrate content varies widely across the Annex IX feedstocks. High-cellulose feedstocks include oat husks (51.3%), miscanthus (42.5%), and sugarcane bagasse (42.5%), which are among the most promising candidates for alcoholysis due to their abundant glucan fractions. Wheat straw also provides a balanced carbohydrate profile (32.1% cellulose, 26.9% hemicellulose), making it an attractive agricultural residue for levulinate production.

By contrast, low-carbohydrate feedstocks such as Sitka spruce (17.8% cellulose, 12.2% hemicellulose) and water hyacinth (16.1% cellulose, 13.1% hemicellulose) are considerably less suitable, as their limited structural carbohydrate fractions constrain theoretical product yields. Brussels sprout residue also exhibits modest carbohydrate levels (19.3% cellulose, 12.0% hemicellulose), further complicated by its unusually high extractives content (41.6%).

Chapter 4. Feedstock Analysis

The relative proportions of hemicellulose also influence conversion behaviour. Bagasse (28.1% hemicellulose) and wheat straw (26.9%) contain significant xylan fractions, which contribute both to levulinate formation and to by-products such as *n*-butyl acetate via cleavage of acetyl substituents (illustrated in Chapter 6). In contrast, oat husks, while exceptionally rich in cellulose, contain comparatively little hemicellulose (7.5%), suggesting that their reactivity will be dominated by glucan hydrolysis rather than xylan-derived products.

Table 8. Biochemical analysis of RED II/RED III ANNEX IX advanced biofuel feedstocks.

Biochemical Analysis of Feedstocks (wt%)												
Feedstock	Cellulose		Hemicellulose				Lignin		Extractives	Ash	Unknown	
	Glucan	Xylan	Arabinan	Galactan	Mannan	Rhamnan	Klason Lignin	Acid-Soluble Lignin				
Corn Cob	29.7	26.9				11.7		23.4	3.1	5.2		
		24.2	2.1	0.5	0.1	0.0	8.6				3.1	
Brussels Sprouts Residue	19.3	12.0				12.7		41.6	9.9	4.5		
		4.8	3.4	2.1	0.8	0.9	10.3				2.4	
Wheat Straw	32.1	26.9				16.7		19.2	4.3	0.8		
		22.9	2.6	0.8	0.4	0.2	14.7				2	
Sugarcane Bagasse	42.5	28.1				19.7		4.4	1.8	3.5		
		25.2	2.1	0.5	0.2	0.1	17.6				2.1	
Peanut Shells	33.2	17.4				25.8		13.9	2.0	7.9		
		15.6	0.7	0.5	0.2	0.4	24.6				1.2	
Oat Husk	51.3	7.5				17.8		17.2	4.2	2.2		
		5.2	1.5	0.7	0.1	0	14.9				2.9	
Beechwood	36.4	21.5				26.5		9.5	0.6	5.6		
		18.6	0.6	0.6	1.3	0.4	23.3				3.2	
Sitka Spruce Thinnings	17.8	12.2				43.0		11.4	10.2	5.4		
		3.1	2.1	2.3	4.3	0.4	41.7				1.3	
Water Hyacinth	16.1	13.1				17.0		21.6	26.8	5.6		
		4.4	5.4	2.3	0.7	0.3	16.3				0.7	
Miscanthus	42.5	21.9				23.2		9.8	1.8	0.7		
		19.9	1.3	0.4	0.2	0.1	21.5				1.7	

Overall, the dataset reveals three broad categories of feedstocks:

1. High-carbohydrate residues and crops (oat husks, miscanthus, bagasse, wheat straw) with strong potential for levulinate yields.
2. Moderate-carbohydrate feedstocks (corn cob, peanut shells, beechwood) where carbohydrate fractions are offset by elevated lignin.
3. Low-carbohydrate, recalcitrant biomasses (Sitka spruce, water hyacinth, Brussels sprout residue) which are compositionally less favourable and likely require pretreatment or harsher conditions.

These distinctions provide a clear basis for predicting feedstock-specific reactivity in subsequent alcoholysis experiments and highlight the value of carbohydrate fractions as primary indicators of conversion potential [32, 106, 216].

4.4.2.3 Lignin Content and Recalcitrance

Lignin is a major determinant of feedstock recalcitrance, as its cross-linked aromatic structure restricts acid penetration, hinders polysaccharide hydrolysis, and contributes to humin formation during alcoholysis [209-211]. In addition, lignin-derived phenolic fragments can condense into inhibitory by-products or consume protons, further reducing catalytic efficiency [212].

The lignin fraction varies widely across the Annex IX feedstocks (Table 8, Figure 30). High-lignin biomasses include Sitka spruce (43.0%), peanut shells (25.8%), and beechwood (26.5%). These materials are particularly recalcitrant, requiring harsher conditions or pretreatment to liberate structural carbohydrates. Their composition favours humin and phenolic by-product formation, consistent with observations in other softwoods and nut shells [27].

Moderate-lignin feedstocks such as wheat straw (16.7%) and sugarcane bagasse (19.7%) represent a more favourable balance between carbohydrate accessibility and structural rigidity. Miscanthus (23.2%) also falls in this category, with lignin levels that can be tolerated under typical alcoholysis conditions. Low-lignin feedstocks such as oat husks (17.8%) and water hyacinth (17.0%) present fewer structural barriers, though their utility is offset by other compositional challenges such as high ash or extractives.

Overall, lignin content provides a strong predictor of recalcitrance: softwoods like Sitka spruce exemplify the upper bound of resistance, while agricultural residues and grasses generally present more manageable levels. This reinforces the need for feedstock-specific optimisation and highlights the dual role of lignin as both a barrier to carbohydrate conversion and a potential source of valorisable aromatic coproducts [209-212].

4.4.2.4 Extractives and Their Influence on Reactivity

Extractives represent a diverse set of non-structural components, including fats, waxes, phenolics, and soluble sugars. Although they typically constitute a minor fraction of biomass, high extractive contents can interfere with acid-catalysed alcoholysis by reacting with intermediates, consuming protons, or diverting pathways toward humin formation rather than productive carbohydrate conversion [213].

The Annex IX feedstocks show substantial variation in extractive levels (Table 8, Figure 30). Outliers include Brussels sprout residue (41.6%) and water hyacinth (21.6%), where extractives approach or exceed structural carbohydrate fractions. Such values are problematic, as extractives are known to exacerbate catalyst deactivation and reduce levulinate yields [33, 207]. Oat husks (17.2%) and peanut shells (13.9%) also contain notable extractive fractions, which may contribute to side reactions if not mitigated. By contrast, bagasse (4.4%), beechwood (9.5%), and miscanthus (9.8%) contain relatively low extractive contents, making them less susceptible to these issues.

While solvent-based pretreatment can remove extractives and improve conversion efficiency, such approaches add cost, complexity, and environmental burden through solvent recovery and waste generation [213]. For this reason, the feedstocks in this study were evaluated in their raw state, reflecting industrially realistic scenarios where extractives must be tolerated or managed in situ.

4.4.2.5 Ash and Inorganic Components

Ash content is another critical factor influencing the suitability of biomass for acid-catalysed alcoholysis. Inorganic constituents, primarily alkali and alkaline earth metals, can neutralise protons and thereby reduce the effective acidity of the reaction medium [214]. This buffering effect decreases levulinate yields, increases catalyst requirements, and can promote the formation of insoluble deposits or tars that complicate downstream processing.

The investigated feedstocks show a broad range of ash contents (Table 8, Figure 30). Water hyacinth (26.8%) and Brussels sprout residue (9.9%) exhibit exceptionally high levels, which substantially reduce their attractiveness as direct feedstocks without pretreatment. Sitka spruce (10.2%) also falls into this category, with high mineral fractions

compounding its already elevated lignin content. By contrast, bagasse (1.8%) and beechwood (0.6%) contain negligible ash levels, underscoring their relative cleanliness and suitability for catalytic processing. Intermediate ash contents are observed in wheat straw (4.3%), miscanthus (1.8%), peanut shells (2.0%), and oat husks (4.2%).

Overall, ash content differentiates feedstocks into those requiring little to no adjustment of catalyst loadings (bagasse, beechwood, miscanthus) and those where substantial buffering must be anticipated (water hyacinth, Brussels sprout residue, Sitka spruce). Inorganic composition therefore represents a practical constraint that must be accounted for in both laboratory optimisation and industrial-scale alcoholysis processes [214].

4.4.2.6 Integrated Compositional–Performance Insights

The biochemical profiles of the Annex IX feedstocks reveal distinct advantages and limitations that will shape their performance under alcoholysis conditions. High-carbohydrate residues and crops such as oat husks, miscanthus, bagasse, and wheat straw are the most promising candidates, combining abundant polysaccharides with manageable levels of lignin, extractives, and ash. These feedstocks are expected to deliver higher alkyl levulinate yields under optimised conditions [32, 106, 216].

Moderate-carbohydrate feedstocks such as corn cob peanut shells and beechwood illustrate a trade-off between carbohydrate availability and elevated lignin content. Their recalcitrance is likely to limit conversion efficiency unless addressed by harsher conditions or selective pretreatments.

Recalcitrant or compositionally challenging feedstocks include Sitka spruce, Brussels sprout residue, and water hyacinth. Sitka spruce combines high lignin (43.0%) and ash (10.2%), Brussels sprout residue contains excessive extractives (41.6%) and ash (9.9%), and water hyacinth has both low carbohydrate content and very high ash (26.8%). These features make them the least favourable feedstocks for direct alcoholysis, though they may still be valorised under tailored process conditions.

The surrogate compounds, glucose, cellulose, and xylan, provide a mechanistic framework for interpreting these compositional trends. Carbohydrate-rich feedstocks can be approximated by glucose and cellulose reactivity, while hemicellulose-rich residues such as

wheat straw and bagasse additionally align with xylan behaviour [124]. Conversely, feedstocks dominated by lignin, extractives, or ash represent deviations from surrogate performance, where side reactions, humin formation, and catalyst neutralisation become more prominent.

Taken together, the integrated analysis establishes a clear ranking of feedstock suitability and underscores the value of surrogate-based modelling in predicting reactivity. This framework provides a strong foundation for the subsequent experimental evaluation of alcoholysis behaviour presented in the following chapter.

While this analysis establishes a comparative framework for Annex IX feedstocks, only a subset of materials were selected for experimental alcoholysis in this study. Specifically, glucose, cellulose, and xylan were chosen as model surrogates of increasing structural complexity, enabling the development of a hierarchical kinetic framework. Corn cob was selected as the representative lignocellulosic biomass due to its balanced carbohydrate composition and its relevance as an agricultural residue. The remaining feedstocks characterised here provide an essential reference dataset and will form the basis of future alcoholysis investigations, beyond the scope of this thesis.

4.4.3 Acetylation of Xylan and Its Implications

Hemicellulose, and in particular xylan, plays a significant role in determining product distributions during alcoholysis. Unlike cellulose, which is a linear homopolymer of glucose, xylan is a branched heteropolymer composed primarily of xylose units substituted with acetyl, arabinosyl, and glucuronosyl side groups. Among these, acetyl substituents are particularly important, as they are readily cleaved under acid-catalysed conditions to release acetic acid or, in alcoholic media, alkyl acetates [190, 191].

The degree of acetylation of xylan was determined using quantitative ^1H NMR spectroscopy under two assumptions. First, each xylopyranose monomer was considered to bear either zero or one acetyl group (monoacetylation assumption). This simplifies the analysis by treating all acetylated monomers as having a single acetyl group, while unacetylated monomers retain both hydroxyl groups. While this assumption may not fully reflect the precise molecular distribution, it provides a robust estimate of the average degree

of acetylation, which is sufficient for predicting product yields in butanolysis reactions. Second, it was assumed that acetyl groups accounted for all substituents in the xylan sample, supported by the absence of signals corresponding to other substituents in the NMR spectra. Minor saccharide side chains such as arabinose were treated as equivalent to additional xylose units for this calculation.

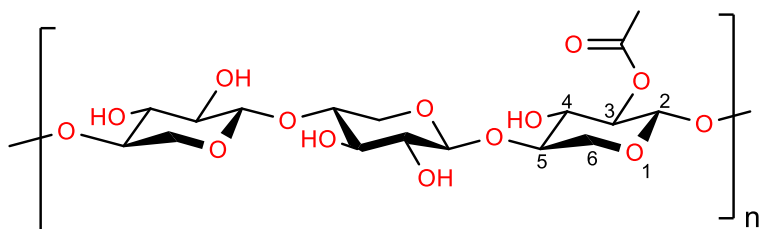


Figure 31. Molecular structure of three linked xylan monomers, two unacetylated (left and central units) and one acetylated at position 3 (right unit).

Table 9 presents the calculation for duplicate analyses, which yielded highly consistent results. The mean monomer-based degree of acetylation was 33.65%, corresponding to a location-based degree of 16.83%. These values confirm that acetyl substituents form a significant structural feature of xylan, validating their role in determining alcoholysis product distributions.

Table 9. Calculations for degree of acetylation for xylan using quantitative ^1H NMR spectroscopy.

Sample	Acetyl Integration	Relative Acetyl Count	OH Integration	Relative Unacetylated Monomers	Monomer-based Acetylation %	Location-based Acetylation %
1	1.0000	0.3333	1.6542	0.6604	33.54	16.77
2	1.0000	0.3333	1.6413	0.6540	33.76	16.88
Mean					33.65	16.83

The mechanistic implications of xylan acetylation extend beyond by-product formation. Cleavage of acetyl groups not only generates acetic acid or alkyl acetates, but also alters hemicellulose solubility, increasing carbohydrate accessibility. At the same time, in situ acetic acid release can accelerate hydrolysis but may also promote side reactions if not carefully controlled. The comparable levels of *n*-butyl acetate observed in reactions with both isolated xylan and corn cob further support the hypothesis that xylan-bound acetyl groups are the dominant source of acetate derivatives in lignocellulosic biomass.

From a surrogate modelling perspective, inclusion of xylan alongside glucose and cellulose is therefore essential to capture these behaviours. Carbohydrate-rich feedstocks

such as wheat straw and bagasse, which contain substantial hemicellulose fractions, are particularly influenced by this pathway, while feedstocks with limited hemicellulose content (e.g. oat husks, Sitka spruce) are less affected. This ensures that surrogate-based predictions of product distributions, including both levulinates and alkyl acetates, accurately reflect the structural chemistry of hemicellulose-rich feedstocks.

4.5 Conclusions

This chapter has provided a detailed elemental and biochemical characterisation of a wide range of Annex IX feedstocks. The results highlight the strong influence of composition on alcoholysis suitability: carbohydrate-rich residues such as oat husks, miscanthus, bagasse, and wheat straw emerge as the most promising candidates for alkyl levulinate production, whereas lignin-rich, extractive-heavy, or ash-rich feedstocks such as Sitka spruce, Brussels sprout residue, and water hyacinth are compositionally less favourable. These findings underscore the importance of comparing feedstock classes across structural carbohydrates, lignin recalcitrance, extractives, and inorganics when assessing their potential for advanced biofuel production.

While this chapter establishes a comparative framework for Annex IX feedstocks, only a subset of materials were taken forward into experimental alcoholysis in this thesis. Glucose, cellulose, and xylan were chosen as surrogates of increasing structural complexity, enabling the development of a hierarchical kinetic framework. Corn cob was selected as the representative lignocellulosic biomass due to its balanced carbohydrate composition and agricultural relevance. The remaining feedstocks characterised here provide an essential dataset for future alcoholysis investigations and form the basis for subsequent PhD projects.

The following chapters build directly on this foundation by evaluating the ethanolysis and butanolysis behaviour of glucose, cellulose, xylan, and corn cob. These experiments quantify product distributions, provide kinetic insights across different levels of structural complexity, and validate the surrogate-based modelling framework established in this chapter.

Chapter 5

Ethanolysis

5.1 Introduction

The global transportation sector, encompassing road, aviation, and maritime applications, remains heavily dependent on fossil-derived fuels, which are a major contributor to anthropogenic greenhouse gas emissions, particularly carbon dioxide (CO₂), a primary driver of climate change [217]. Biofuels represent a viable pathway to decarbonisation, as many can be integrated within existing engines and infrastructure without significant modification. However, large-scale deployment of conventional biofuels has been hindered by competition with food production and indirect land-use impacts associated with cultivating first-generation feedstocks.

Advanced biofuels derived from waste, residues, and non-food lignocellulosic materials offer a more sustainable alternative. The revised Renewable Energy Directive (RED III) explicitly identifies lignocellulosic biomass as a priority Annex IX feedstock [27], owing to its abundance, by-product designation, and favourable sustainability profile. Yet, the intrinsic recalcitrance of lignocellulose, combined with its high oxygen content, continues to complicate conversion into energy carriers with properties comparable to petroleum fuels [218, 219].

A range of thermochemical routes has been explored for lignocellulose valorisation, including hydrolysis [220], alcoholysis [66], pyrolysis [221], gasification [222], hydrothermal liquefaction [223] and hydrothermal carbonisation [224]. Among these, acid-catalysed alcoholysis, referred to as ethanolysis when ethanol is used as solvent, remains comparatively underexplored. Ethanolysis enables the direct conversion of carbohydrate

fractions into alkyl levulinates, most notably ethyl levulinate, while simultaneously producing diethyl ether, ethanol, water, and small quantities of formic acid. Ethyl levulinate, ethanol and diethyl ether have been identified as a potential drop-in fuel components in their own right [35, 198, 225], though their individual blending limits with hydrocarbon fuels restrict direct use.

Recent studies have shown that mixtures of ethyl levulinate, diethyl ether, and ethanol can deliver combustion and ignition properties superior to those of the pure components, offering the possibility of tuneable, advanced biofuel blends [122, 225]. Beyond their fuel applications, alkyl levulinates are valued as versatile platform chemicals, serving as solvents, flavouring agents, and precursors to bio-based polymers and γ -valerolactone [35, 198].

Despite its potential, ethanolysis research is constrained by inconsistent methodologies. Reported yields are often taken at arbitrary reaction times, with limited distinction between kinetic and steady-state regimes. Furthermore, diethyl ether formation is frequently ignored, even though it directly affects ethanol utilisation and process economics [37, 46, 47, 61, 122]. These limitations hinder both meaningful cross-study comparison and the development of robust kinetic or techno-economic models.

This chapter addresses these gaps by systematically investigating the steady-state ethanolysis of glucose, cellulose, and corn cob under sulphuric acid catalysis. It quantifies ethyl levulinate and diethyl ether yields, establishes steady-state performance benchmarks, and develops a hierarchical kinetic model that bridges laboratory-scale experiments with process-level understanding.

5.1.1 Background and Literature Context

Alcoholysis, and specifically ethanolysis, has been comparatively underexplored despite offering a direct route to alkyl levulinates, most notably ethyl levulinate when ethanol is used as solvent. The techno-economic performance of ethanolysis has been rigorously evaluated. In their assessment of 148 process scenarios, Silva et al. [37] identified 53 as commercially promising, highlighting three consistent findings: (i) sulphuric acid was the only catalyst in viable processes, (ii) ethanol accounted for approximately 38% of total production costs, and (iii) biomass contributed around 34%. These insights underline the

importance of atom-efficiency in both solvent and feedstock utilisation and explain why more complex catalyst systems remain economically uncompetitive at scale.

Despite a growing body of work, ethanolysis research remains fragmented. Reported product yields are often measured at arbitrary reaction times rather than at steady-state, leading to inconsistent benchmarks across studies. Moreover, maximum ethyl levulinate yields are frequently pursued without sufficient consideration of by-product formation or process techno-economics. This has led to a tendency to operate at low feedstock loadings in order to maximise ethyl levulinate yield, a practice that is counterintuitive in light of the findings of Silva et al. [37], who demonstrated that biomass and ethanol together account for over 70% of process costs (34% and 38% respectively). These results suggest that processes achieving comparable maximum yields at higher feedstock loadings should instead be prioritised. Co-product formation, particularly diethyl ether, is also often neglected, despite its direct impact on ethanol utilisation and overall process efficiency. Finally, kinetic and mechanistic models for real biomass systems remain limited, restricting the ability to perform cross-study comparisons, construct predictive frameworks, or generate robust techno-economic assessments.

This thesis addresses these gaps by systematically quantifying steady-state ethanolysis of both model (glucose, cellulose) and real (corn cob) feedstocks. By explicitly accounting for ester, ether, and by-product formation, and by developing a hierarchical kinetic model, this work establishes a more complete basis for evaluating ethanolysis as a pathway to advanced biofuels.

5.1.2 Fuel Properties and Applications

5.1.2.1 Advanced Biofuel Blends

Ethyl levulinate has been widely investigated as a potential biofuel component for both diesel and gasoline engines, owing to its oxygen content, miscibility, and relatively clean combustion profile [35, 198, 225]. However, ethyl levulinate on its own suffers from limitations, including restricted blending ratios in diesel and relatively low ignition quality compared to petroleum-derived fuels [122].

The ethanolysis process is distinct in that it generates not only ethyl levulinate but also diethyl ether and while also containing unreacted ethanol, yielding a ternary product mixture with complementary fuel properties. Diethyl ether, with its high cetane number and volatility, functions as a powerful ignition promoter, while ethanol contributes high octane properties that enhance spark-ignition performance [40]. The resulting blends therefore integrate the strengths of each component.

Howard's doctoral work demonstrated that mixtures of ethyl levulinate, diethyl ether, and ethanol can be tuned to achieve derived cetane numbers between 10 and 130, effectively spanning both gasoline and diesel combustion regimes [51]. Similarly, Wiseman showed that alcoholysis-derived ternary blends could be incorporated into diesel at up to 25 vol% while remaining compliant with major fuel standards, with butyl-based analogues exhibiting especially favourable performance and emissions reductions [40]. These findings highlight the potential of alcoholysis products not as isolated molecules but as versatile, drop-in blending agents capable of tailoring fuel properties for multiple engine types.

5.1.2.2 Beyond Fuels

Beyond their application in fuels, alkyl levulinates possess significant value as platform chemicals. Ethyl levulinate is already employed as a flavouring and fragrance additive, a green solvent, and a precursor to higher-value derivatives such as γ -valerolactone and bio-based polymers [35, 198]. This multifunctionality enhances the appeal of ethanolysis within a biorefinery framework, where the co-production of fuels and chemicals can improve overall process economics and resilience.

Policy frameworks further reinforce the importance of dual-use feedstocks and products. Under RED II/RED III, lignocellulosic biomass is identified as a sustainable Annex IX feedstock [27], with strong incentives for its conversion into advanced biofuels. The ability of ethanolysis to deliver both drop-in fuel mixtures and platform chemicals therefore aligns with regulatory priorities, offering a pathway that is both environmentally and economically strategic.

5.1.3 Mechanistic Pathways of Ethanolysis

The ethanolysis of lignocellulosic biomass proceeds through a complex network of acid-catalysed reactions, with cellulose and its monomer glucose as the primary carbohydrate precursors. The global reaction pathway is often simplified to describe the conversion of glucose to ethyl levulinate in the presence of ethanol and sulphuric acid [14]. In practice, this process involves sequential steps of ethanolysis and dehydration, leading to the formation of ethyl glucosides, and ultimately ethyl levulinate via esterification [14,57,58]. For real biomass feedstocks, hemicellulose-derived pentoses also contribute to ethyl levulinate formation, although with lower efficiency [62–64].

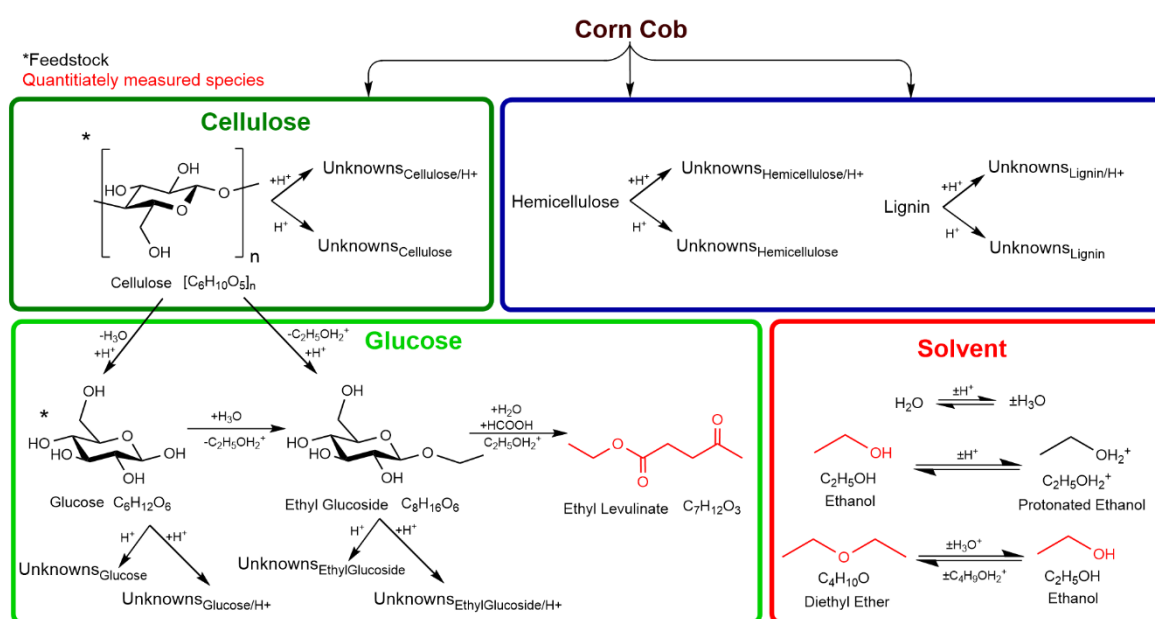


Figure 32. Hierarchical biochemical surrogate kinetic model for ethanolysis, illustrating the proposed reaction mechanism and hierarchical sub-models. Associated reaction equations are provided in Table 14. Unknown species are inferred by mass balance and encapsulate both soluble and insoluble unidentified species.

A major competing reaction is the acid-catalysed dehydration of ethanol to diethyl ether. While diethyl ether possesses favourable combustion properties, its formation consumes ethanol and generates water, reducing both solvent efficiency and ester yields [14,55,56]. The extent of diethyl ether production is highly dependent on acid concentration and temperature, yet it has often been neglected in ethanolysis studies. Howard's mechanistic modelling emphasised that ethanol dehydration can dominate under conditions otherwise optimised for ethyl levulinate production, highlighting the trade-off between ester and ether pathways [51].

Humins represent another unavoidable side-product. These insoluble carbonaceous solids form through the polymerisation of reactive intermediates such as hydroxymethyl furfural, Ethoxymethylfurfural or furfural [57,58]. Although ethanol suppresses humin formation relative to aqueous hydrolysis, humins remain a significant sink for carbon, lowering overall conversion efficiency and complicating process design. Structural analyses suggest that humins generated in ethanol may incorporate ethoxy groups, differentiating them from their aqueous counterparts [57].

The composition of ethanolysis product mixtures, typically ethyl levulinate, diethyl ether, ethanol, water, and humins, has direct implications for downstream utilisation. Wiseman's engine testing of alcoholysis-derived ternary blends demonstrated that diethyl ether content enhanced cetane number and ignition quality, even as its formation reduced overall ethanol efficiency [41]. This dual role illustrates the central challenge of ethanolysis: optimising competing reaction pathways to balance process efficiency with desirable end-use fuel properties.

Taken together, these mechanistic insights underscore the importance of considering full product distributions when assessing ethanolysis. Quantifying esters, alcohols, ethers and humins in tandem, rather than focusing solely on ethyl levulinate, is essential to evaluating the true viability of the process and forms the foundation for the steady-state analysis presented in this chapter.

5.1.4 Importance of Achieving Steady-State

A persistent limitation in the ethanolysis literature is the inconsistent treatment of yield. Many studies report ethyl levulinate at single, arbitrary times without distinguishing transient kinetics from the time-invariant composition [106, 107, 111, 113, 115-117, 135, 136]. Apparent maxima then reflect sampling time rather than the intrinsic process potential, frustrating cross-study comparison and hindering robust kinetic or techno-economic models.

In this context, steady-state is defined as the earliest time at which product concentrations no longer vary within experimental uncertainty. It is a kinetic condition, not full thermodynamic equilibrium, but it does approximate a local free-energy minimum for the accessible pathways under the chosen conditions. Quantifying steady-state mixtures also

allows complete carbon and alcohol balances, incorporating ethyl levulinate, diethyl ether, water, and humins. These balances are critical for techno-economics, since solvent utilisation and feedstock efficiency dominate process costs [37].

Quantifying steady-state mixtures also allows complete carbon and alcohol balances, incorporating ethyl levulinate, diethyl ether, water, and humins. These balances are critical for techno-economics, since solvent utilisation and feedstock efficiency dominate process costs [51]. Engine testing further confirms that ignition quality and emissions depend directly on the final balance of ethyl levulinate, diethyl ether, and residual alcohols [40].

For these reasons, steady-state yields provide the only meaningful benchmark for evaluating ethanolysis as a pathway to advanced biofuels. This thesis therefore adopts steady-state as the standard basis for reporting ethanolysis outcomes, ensuring that comparisons across feedstocks and conditions reflect the maximum attainable performance.

5.2 Objectives of Ethanolysis Study

The objectives of this chapter were fivefold:

1. To define steady-state in ethanolysis reactions by establishing the point at which product concentrations cease to change with time, thereby providing a rigorous benchmark for meaningful yield comparison.
2. To quantify the yields of ethyl levulinate, diethyl ether, and other co-products at steady-state across glucose, cellulose, and corn cob, enabling a complete carbon and alcohol balance of the process.
3. To determine the effect of feedstock loading and acid concentration on ethanolysis outcomes, clarifying whether the process is truly catalytic under varying biomass-to-acid ratios.
4. To develop and validate a hierarchical surrogate kinetic model spanning glucose, cellulose, and lignocellulosic biomass, capable of capturing increasing structural complexity and reproducing experimental trends.
5. To benchmark ethanolysis performance against literature reports, providing a coherent comparative framework for evaluating process potential and techno-economic implications.

In pursuing these objectives, further unanticipated findings emerged that prompted additional analyses. These revealed important mechanistic features of the ethanolysis process and expanded the scope of the conclusions, highlighting aspects of catalyst behaviour and hemicellulose reactivity not originally envisaged at the outset. Together, the planned objectives and these emergent insights establish a robust experimental and modelling framework for evaluating ethanolysis as a pathway to advanced biofuels.

5.3 Methodologies Employed

The ethanolysis experiments presented in this chapter were conducted using Alcoholysis Procedure – Method A (Section 3.3.1). Feedstock, ethanol, and sulphuric acid were combined in sealed 15 mL pressure tubes (total mass 5 g) and heated at 150 °C for the specified reaction time. After cooling, the reaction mixtures were centrifuged, neutralised with sodium hydrogen carbonate (50 mg), and diluted in dimethyl sulfoxide (400:1 solvent-to-sample ratio) prior to gas chromatography analysis (Section 3.4.1). All experiments were performed in duplicate with analytical replicates, giving four data points per condition; uncertainties are reported as one standard deviation.

A central methodological focus was the determination of steady-state, defined as the earliest time at which product yields no longer varied within experimental uncertainty. This ensured that reported yields of ethyl levulinate and diethyl ether reflected maximum attainable values rather than transient outcomes at arbitrary timepoints.

Kinetic modelling was performed using the Ethanolysis Surrogate Kinetic Model (Section 3.7.3.1). This hierarchical framework incorporated glucose, cellulose, and corn cob submodels, parameterised using the compositional analysis reported in Chapter 4. Parameters were constrained by steady-state experimental data obtained under Method A conditions, providing a chemically consistent description of competing ester and ether pathways.

5.4 Results and Discussion

5.4.1 Steady-States of Glucose, Cellulose, and Corn Cob Ethanolysis

The steady-state times, concentrations, and yields of ethyl levulinate recorded for the sulphuric acid-catalysed (0.5 wt.%) ethanolysis of glucose, cellulose, and corn cob at 5, 10, and 20 wt.%, at 150 °C, are listed in Table 10.

Table 10. Steady-States of Ethyl Levulinate Production.

Steady-States of Ethyl Levulinate (EL) Production					
Feedstock	Acid Loading (wt.%)	Feedstock Loading (wt.%)	Steady-State Mass of EL (g)	EL Yield (wt.%)	Steady-State Times (mins)
Glucose	0.5	5	0.12 ± 0.01	46.6 ± 3.7	500-1000
		10	0.23 ± 0.01	45.0 ± 2.7	
		20	0.40 ± 0.07	40.4 ± 6.7	
Cellulose	0.5	5	0.13 ± 0.01	50.2 ± 5.4	1000-2000
		10	0.24 ± 0.03	48.3 ± 5.7	
		20	0.39 ± 0.08	38.9 ± 7.5	
Corn cob	0.5	5	0.07 ± 0.01	27.0 ± 1.9	2000-3000
		10	0.11 ± 0.01	21.4 ± 2.7	
		20	0.06 ± 0.02	6.3 ± 1.5	
	2.0	20	0.20 ± 0.05	19.6 ± 4.8	2000-3000

Average steady-state masses, average steady-state yields and time taken to reach steady-state for ethyl levulinate production via sulphuric acid catalysed ethanolysis (according to the previously defined conditions to achieve steady-state) for the three loadings of each of the three feedstocks at 150 °C. Uncertainty = 1 standard deviation.

Because of the chemical complexity, the observed steady-state times of ethyl levulinate's production are the following glucose 500–1000, cellulose 1000–2000, corn cob 2000–3000 minutes. This trend is integrated into the construction of the kinetic model in the form of sub-models. For a given reaction time and initial concentration of the feedstock, the concentration of ethyl levulinate formed is observed to be dependent on the feedstock type. The concentration of ethyl levulinate obtained from the alcoholysis of glucose and cellulose is approximately double that obtained from corn cob. This yield of ethyl levulinate from corn cob is higher than that predicted based on the cellulose content of the corn cob and the experimentally determined ethyl levulinate yields from pure cellulose. This discovery indicates that ethyl levulinate may also be derived from other constituents of the

lignocellulosic biomass and challenges the common assumption that all ethyl levulinate produced from the alcoholysis of real-world biomass is derived from its cellulose content.

The highest average steady-state concentrations of ethyl levulinate produced from the ethanolysis of glucose and cellulose are achieved at the highest mass loading of the feedstock (20 wt.%): (0.40 ± 0.07) g, i.e., (40.4 ± 7.3) wt.% yield, and (0.39 ± 0.06) g, i.e., (38.9 ± 6.1) wt.% yield, respectively. A clear dependence is observed between the ethyl levulinate (g) formed and the initial mass loading of the feedstock for both glucose and cellulose. Surprisingly, this trend is not observed for corn cob, a real-world lignocellulosic biomass.

The amount of ethyl levulinate produced from the ethanolysis of corn cob, with 0.5 wt.% acid, scales linearly with the initial mass loading of feedstock until some critical value above 10 wt.% of feedstock. Initially, the maximum steady-state concentration achieved for corn cob is (0.10 ± 0.02) g, i.e., (20.3 ± 3.5) % yield, by utilizing 0.5 wt.% of acid at 10 wt.% of feedstock. Conversely, the ethyl levulinate formed for 20 wt.% of corn cob was only (0.06 ± 0.02) g, i.e., (6.3 ± 1.5) % yield. This is hypothesised to be triggered by the changing feedstock to acid ratio, as the sulphuric acid concentration is kept constant (0.5 wt.%). Therefore, an additional time-dependent data set for corn cob (20 wt.%) with a higher acid concentration (2 wt.%) is performed to improve the yield of ethyl levulinate, leading to (0.20 ± 0.05) g, i.e., 19.6 ± 4.8 % yield. This shows that the ethyl levulinate production from corn cob requires the acid concentration to be scaled with the biomass concentration, indicating that the process is not fully catalytic. To investigate the catalytic nature of lignocellulosic alcoholysis, another set of acid-dependent experiments are performed and are discussed in the next section.

The highest average steady-state yields of ethyl levulinate produced from the ethanolysis of glucose (46.6 ± 3.7) , cellulose (50.2 ± 5.4) , and corn cob (27.0 ± 1.9) % are achieved at 5 wt.% feedstock, 0.5 wt.% sulphuric acid, and 94.5 wt.% ethanol at 150 °C. Notably, the yield of ethyl levulinate decreases as the feedstock loading increases. This trend tends to result in studies configuring a lower feedstock concentration relative to the ethanol and acid concentrations to achieve maximum yields of ethyl levulinate. It is important to appreciate the techno-economic realities when considering the commercialisation of such a process. While lower feedstocks loadings may result in higher ethyl levulinate yields, this also results in greater use and consumption of the costly alcohol, which accounts for approximately 38% of the total process [37].

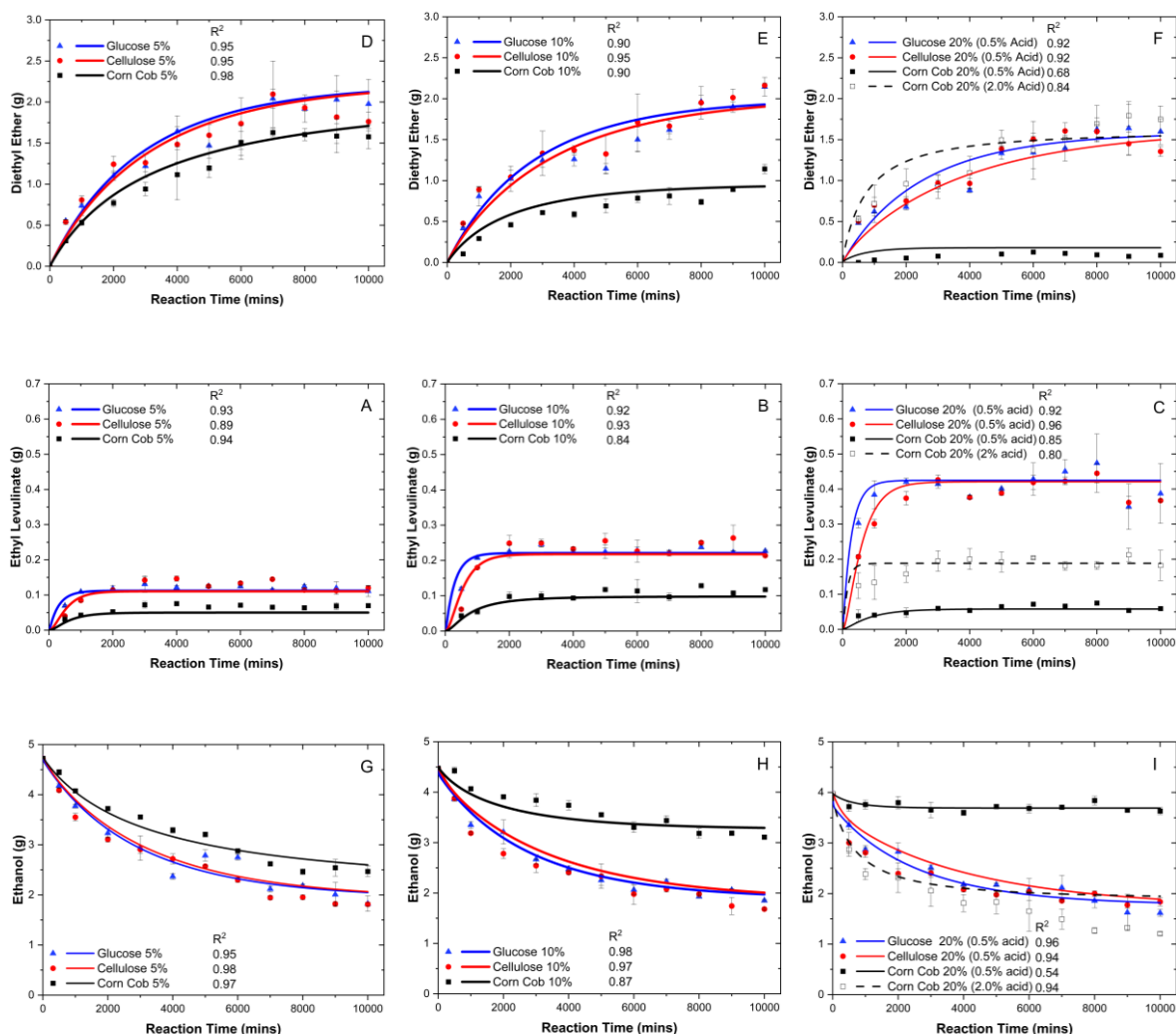


Figure 33. Ethyl levulinate (g)[A, B, and C], diethyl ether (g)[D, E, and F], and ethanol (g)[G, H, and I] concentrations present in the product mixture produced from the sulphuric acid-catalysed ethanolysis of glucose, cellulose, and corn cob (5, 10, and 20 wt.%) at 150 °C. The data points represent the average of 4 experimental data points, while the uncertainties are the standard deviation of those 4 points. The lines are produced by the surrogate kinetic model.

This trend is amplified for corn cob as there is a significant drop in ethyl levulinate yield as the feedstock loading increases. The yield drops from 27.0 to 6.3 % at 5 and 20 wt.% of corn cob, respectively. This indicates that protons are irreversibly consumed at higher concentrations of biomass relative to the sulphuric acid, preventing the reaction from proceeding. These findings are illustrated in Figure 33. “This hypothesis is further evidenced by the quantities of diethyl ether present in the reaction mixture. For glucose and cellulose, a small drop in diethyl ether production is observed, as the feedstock loading increases. This is due to the decrease in concentration of ethanol in the reaction as the formation of diethyl ether is both a function of initial acid and ethanol concentrations. Therefore, a small drop in diethyl ether production is expected for these reaction conditions. However, at 20 wt.% of

corn cob, a negligible quantity of diethyl ether is produced. This again indicates that for the real lignocellulosic biomass, corn co

5.4.2 Effect of Acid Concentration on Yields

A series of experiments are performed to determine the effect of acid concentration on the alcoholysis of biomass to produce ethyl levulinate at three different feedstock:acid ratios (10:1, 20:1, and 40:1) and feedstock loadings (5, 10, and 20 wt.%) for glucose, cellulose, and corn cob; see Table 11. Two sets of experiments are carried out to evaluate the catalytic nature of this system at a constant mass mixture of 5 g: one at steady-state conditions (reaction time of 6000 minutes) and one at kinetic phase conditions (reaction time of 1000 minutes), as shown in Figure 34.

Table 11. Acid-dependent study of ethyl levulinate production at 6000 minutes at 150 °C.

Acid-Dependent Ethyl Levulinate Yields (wt.%)				
Feedstock	Feedstock (wt.%)	Feedstock:Acid Mass Ratio		
		10:1	20:1	40:1
Glucose	5	46.5 ± 1.7	53.4 ± 6.1	45.4 ± 10.3
	10	41.6 ± 2.5	43.4 ± 5.7	51.3 ± 12.7
	20	41.7 ± 2.6	41.5 ± 5.4	39.4 ± 1.8
Cellulose	5	49.2 ± 2.1	51.0 ± 4.1	40.7 ± 5.8
	10	43.0 ± 1.5	42.9 ± 1.3	53.3 ± 18.5
	20	43.1 ± 3.1	39.9 ± 4.1	41.4 ± 1.0
Corn cob	5	26.2 ± 2.2	13.0 ± 1.0	3.7 ± 1.4
	10	23.9 ± 4.0	22.4 ± 4.6	5.8 ± 0.4
	20	20.6 ± 5.3	18.9 ± 0.2	6.4 ± 0.3

Temperature= 150 °C, Uncertainty = 1 standard deviation.

Yields (wt.%) of ethyl levulinate produced from the sulphuric acid-catalysed ethanolysis of glucose, cellulose, and corn cob (5, 10, and 20 mass percent) for three different feedstock-to-acid ratios (10:1, 20:1, and 40:1) at 150°C for a reaction time of 6000 minutes. Four experiments are performed for each data point, and the uncertainty is the standard deviation of those four points.

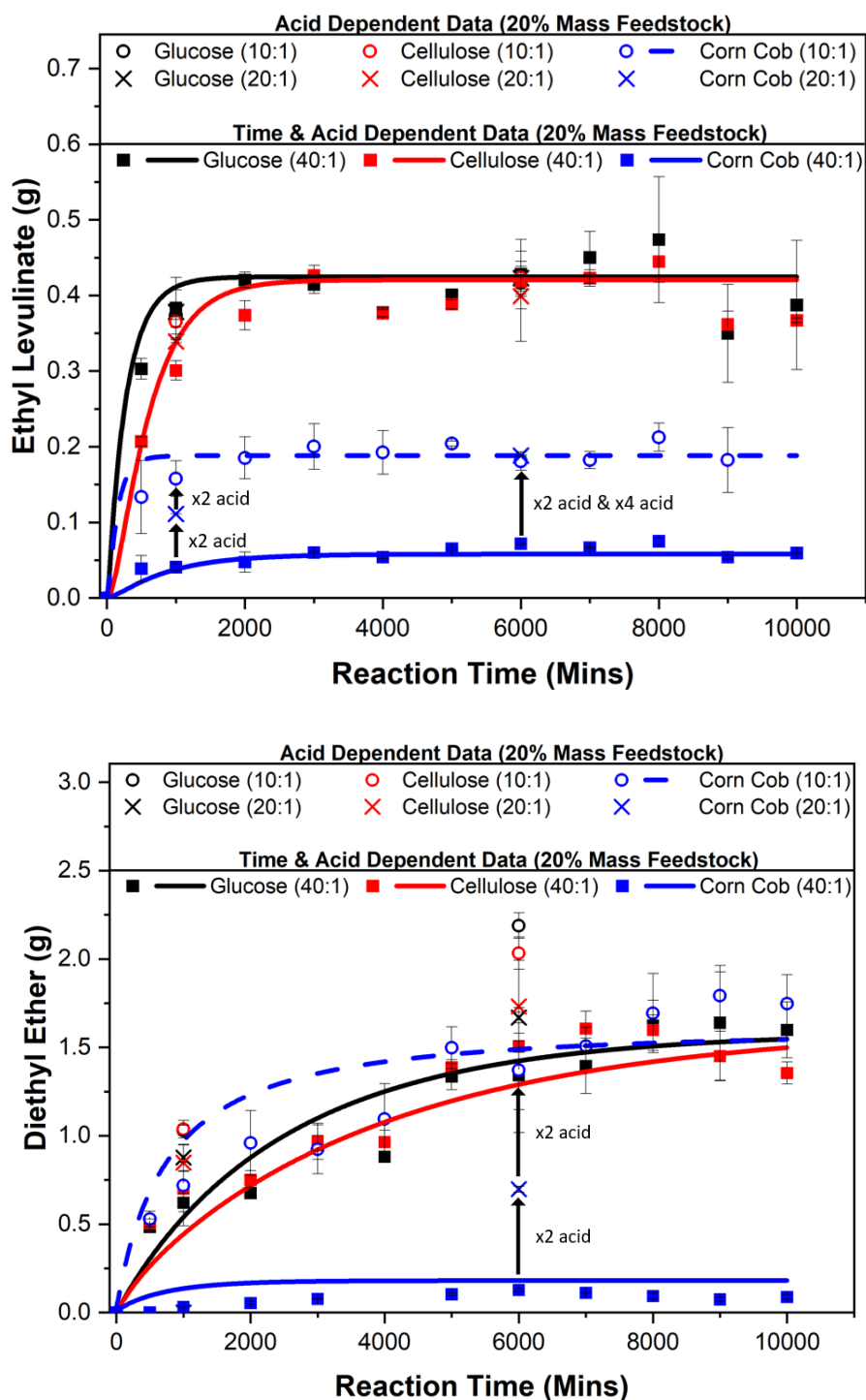


Figure 34. Ethyl levulinate and diethyl ether yields (g) from sulphuric acid-catalysed ethanolysis of glucose, cellulose, and corn cob (5, 10, 20 wt.%) at 150 °C across feedstock-to-acid ratios of 10:1, 20:1, and 40:1. Full time-dependent profiles are shown for a 40:1 ratio, with an additional profile for corn cob at 10:1. Reactions at 1000 and 6000 minutes explore acid dependence at all three ratios during kinetic and steady-state phases. Squares, crosses, and circles denote experimental data; lines denote model predictions.

At 6000 minutes, when the reaction is at steady-state, the amount of ethyl levulinate formed from glucose and cellulose is independent of the acid concentration. This is also true for glucose at 1000 minutes, as this reaction has reached its steady-state at this point. This further supports the catalytic features of this process driven by the regeneration of protons.

However, for cellulose at 1000 minutes, the reaction is still in the kinetic phase, meaning that the steady-state has not been reached. At this point, the ethyl levulinate formed is dependent on the acid concentration, indicating that the concentration of acid appears to only affect the rate of the reaction but not the concentration of ethyl levulinate in steady-states.

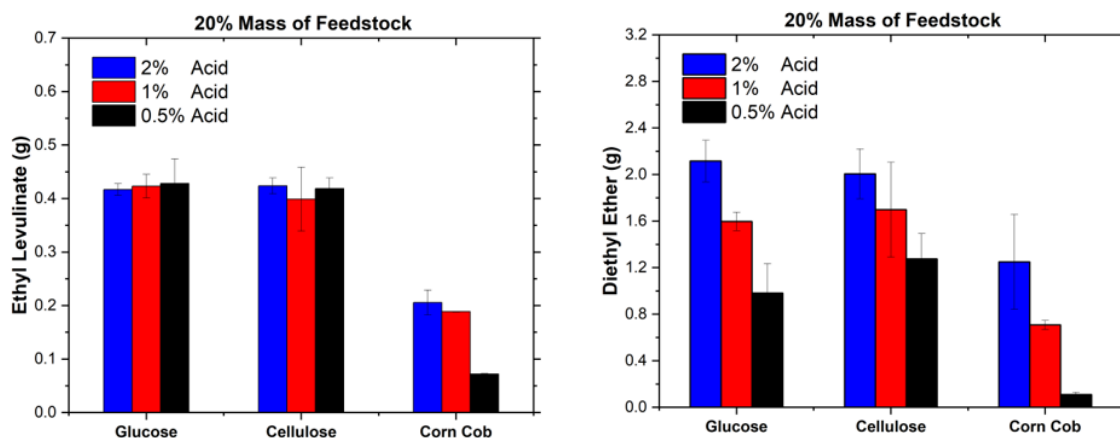


Figure 35. Ethyl levulinate (g) and diethyl ether (g) produced from the sulphuric acid-catalysed ethanolysis of glucose, cellulose, and corn cob (5, 10, and 20 wt.%) for three different acid concentrations (0.5, 1 and 2 wt.%) for a reaction time of 6000 minutes at 150°C.

For corn cob at 6000 minutes the amount of ethyl levulinate formed is dependent on the concentration of acid until some critical value. At a feedstock:acid ratio of 40:1, the amount of ethyl levulinate and diethyl ether is negligible, evidencing the population of protons is too low to catalyse the reaction as they are consumed via an unexplored mechanism. Diethyl ether is an unavoidable co-product in the acid-catalysed ethanolysis of biomass. As shown in Figure 35, the produced amount of this species is dependent on the acid content added to the system. It is, therefore, desirable to use the minimum concentration of acid necessary in order to minimise diethyl ether production. The determination of this minimum concentration for the case of sulphuric acid is essential for the techno-economic-analysis of such a process. For corn cob at 150°C, this feedstock:acid ratio is in the range of 10:1 to 20:1.

The observed loss of catalytic activity at high feedstock-to-acid ratios suggests that protons are irreversibly consumed during ethanolysis. To clarify the fate of the sulphuric acid catalyst under these conditions, the elemental composition of humins was examined in order to track sulphur partitioning.

5.4.3 Fate of the Sulphuric Acid Catalyst

An outstanding question in ethanolysis is the fate of the sulphur introduced as sulphuric acid catalyst. This has both mechanistic and practical relevance, as residual sulphur in liquid fuel fractions is undesirable and subject to strict regulatory limits. To address this, the elemental composition of humins derived from corn cob and cellulose was determined at varying feedstock-to-acid ratios and reaction times (Table 12).

Table 12. Ultimate Analysis of humin samples on a dry basis.

Reaction Conditions				Elemental Analysis (wt.%)				
Feedstock	Feedstock Loading (wt.%)	Reaction Time (mins)	Feedstock /Acid ratio	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen
Corn cob	20	10000	10	55.5 ± 3.5	4.1 ± 0.2	1.1 ± 0.02	4.7 ± 0.1	25.5 ± 3.8

Reported values correspond to the mean of the analyses performed, with the associated uncertainty given as the standard deviation of the measurements.

Elemental analysis revealed that the sulphur content of humins increased with decreasing feedstock-to-acid ratio, reaching up to 4.7 wt.% at 10:1 ratios after prolonged reaction times. For the case of corn cob at 20 wt.% loading, 2 wt.% H₂SO₄ in a 5 g reaction mixture corresponds to 0.10 g of sulphuric acid initially present. At 10,000 minutes, the humins recovered contained 0.65 g total mass with 4.71 wt.% sulphur, equivalent to 0.031 g sulphur. This corresponds to ≥93.9% of the initial sulphur content, within the uncertainty of humin mass recovery.

These results indicate that the overwhelming majority of the sulphur from H₂SO₄ becomes incorporated into the solid humin fraction, most likely as sulfonated functionalities. This finding corroborates earlier literature suggestions that proton consumption during biomass ethanolysis is irreversible at high feedstock loadings. Importantly, gas chromatographic analysis of the liquid phase confirmed the absence of sulphur-containing species, consistent with sulphur retention in the humins.

From a process perspective, this partitioning has two consequences. First, it mitigates concerns over sulphur contamination in the liquid fuel products, provided that humins are removed prior to downstream upgrading. Second, it suggests that sulphuric acid is not fully catalytic in lignocellulosic ethanolysis but is consumed via incorporation into humins, thereby reducing effective proton availability. This explains the strong acid dependence

observed at high biomass loadings and further underscores the need for careful optimisation of catalyst dosage relative to feedstock concentration.

5.4.4 Ethanolysis of Hemicellulose-Derived Xylan

To further investigate the origin of the additional ethyl levulinate yield observed in corn cob beyond that predicted from its cellulose content, ethanolysis experiments were extended to hemicellulose-derived xylan. Hemicellulose is a heterogeneous polysaccharide composed primarily of pentoses, including xylose, arabinose, mannose, and galactose, with xylan typically identified as the dominant constituent in grasses such as wheat straw and corn stalks. Puitel et al. reported that the hemicellulose fraction of wheat straw and corn cob consists of 88–93% xylan, confirming its central role in these biomasses [2].

Figure 36 shows the repeating monomer of anhydrous xylose which forms the main backbone of xylan [126]. Under the acid-catalysed ethanolysis conditions employed here, xylan achieved an average ethyl levulinate yield of 8.9 ± 1.6 wt.% at steady-state. This confirms that hemicellulose, specifically its xylan component, can serve as a direct precursor to alkyl levulinate formation via alcoholysis.

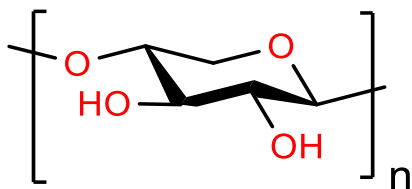


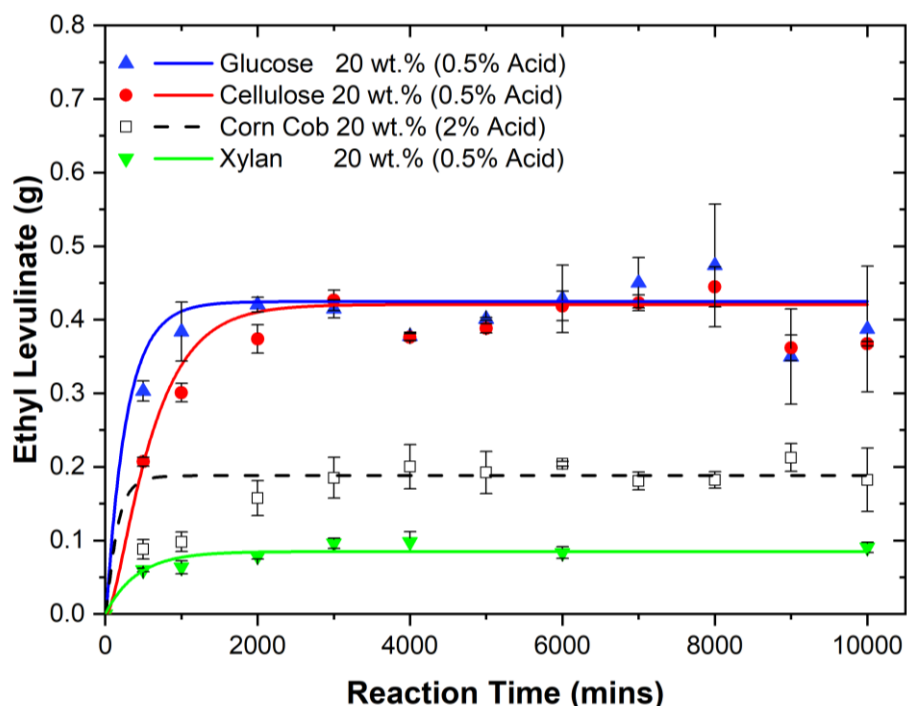
Figure 36. Structure of anhydrous xylose, the principal monomeric unit of xylan [124].

Comparison of ethyl levulinate yields across feedstocks (Table 10) shows that while glucose and cellulose achieved steady-state yields of approximately 40–50 wt.%, xylan produced significantly lower yields. However, its contribution helps explain the discrepancy between predicted and measured ethyl levulinate yields for real lignocellulosic feedstocks such as corn cob, which contains a substantial hemicellulosic fraction.

To the best of our knowledge, this is the first demonstration that hemicellulose can produce alkyl levulinates directly via ethanolysis. This novel finding extends the range of lignocellulosic fractions that can be valorised through alcoholysis, challenging the prevailing assumption that levulinate formation derives exclusively from cellulose. Xylan will

therefore be included as a feedstock in subsequent butanolysis studies, enabling a systematic evaluation of hemicellulose contributions to alkyl levulinate formation across different alcohol solvents.

Figure 37. Ethyl levulinate (g) produced from the sulphuric acid-catalysed ethanolysis of glucose, cellulose, xylan and



corn cob at 150 °C.

5.4.5 Comparison with Literature

Numerous studies have detailed the acid-catalysed hydrolysis of carbohydrates in other alcohols in a one-pot system. These reports were recently addressed in a comprehensive review by Galletti and co-workers [66]. Figure 12, Figure 13 (from Section 2.3.3) and Figure 38 (shown here) analyse the yields of ethyl levulinate reported by literature studies as a function of (i) catalyst type, (ii) reaction temperature, and (iii) feedstock type, respectively. Figure 13 (Chapter 2) and Figure 38 (below) only consider glucose as the feedstock, and thus, all yields have been converted to molar yields based on Equation 13. Figure 12 (Chapter 2) compares real-world biomass, and therefore, all yields are converted to mass yields, consistent with all yields reported in this work.

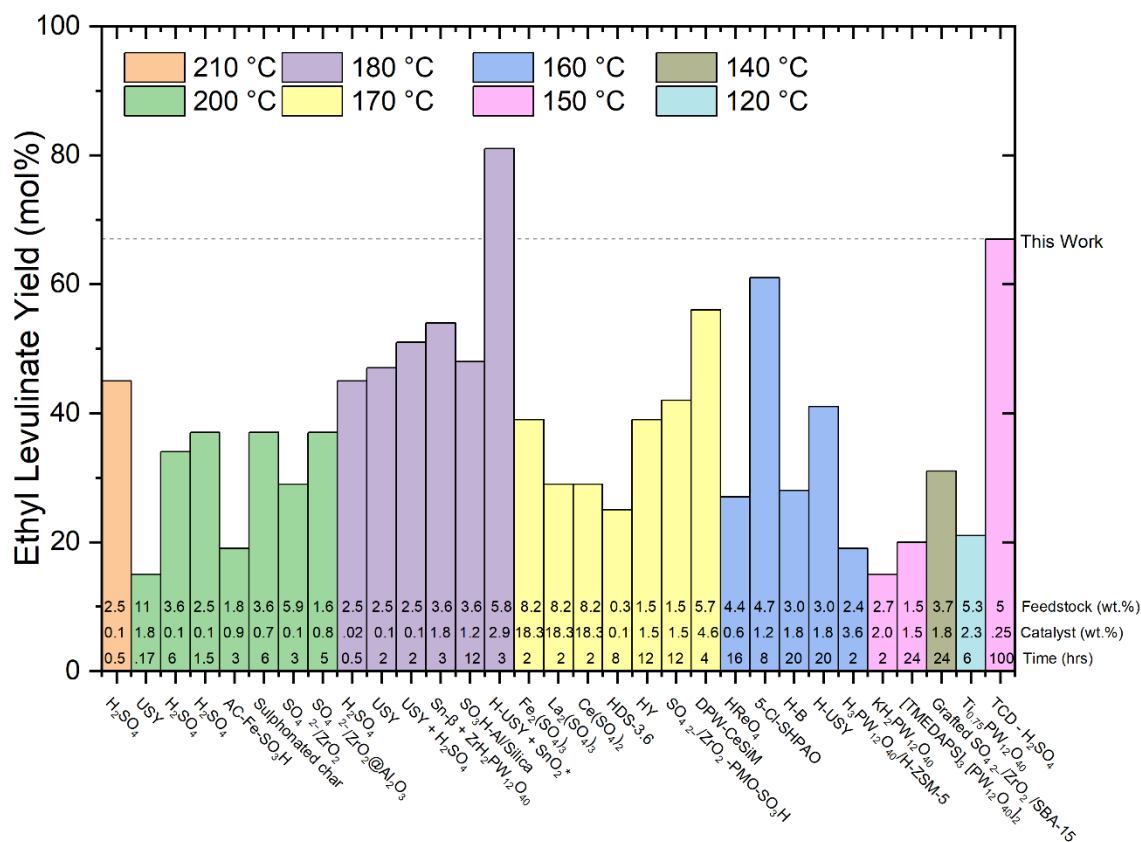


Figure 38. Literature review of experimental yields of ethyl levulinate using various catalyst types [52, 58, 68-70, 72-75, 78-88, 125, 133, 137, 138]. All reaction systems use conventional heating and a one-pot process. The feedstock loading (wt.%), catalyst loading (wt.%), and reaction times are displayed at the bottom of each column.

On examination of the literature in this way, it is clear that there has been no coherent overarching attempt to systematically study the reaction conditions with a view to understanding their influence on the rate and/or yield of ethyl levulinate. Rather, the studies are more of a stand-alone nature, resulting in an unorganised ensemble of experimental parameters and associated observations. This sort of ensemble may lend itself to mathematical analysis such as multiple linear regression, or principal component analysis, whereby the dependence of a performance variable (ethyl levulinate concentration) is delineated with respect to each parameter of an ensemble. In this example, the ensemble would be catalyst type, catalyst concentration, reaction temperature, feedstock type, feedstock concentration, and importantly, reaction time. Efforts to form an accurate multiple linear regression model for this literature data produced a low-quality model. This is due to

too wide a variability in experimental parameters, and insufficient experimental data. The model is provided in the appendix of this thesis.

Though an entirely objective numerical assessment of the importance of each parameter is, at the moment inconclusive, even with the wide variability in conditions studied, given the data available, we believe that the following basic statements are essentially true.

1. Longer reaction times achieve higher ethyl levulinate “yields”, until the steady-state of ethyl levulinate production has been achieved.
2. Higher reaction temperatures achieve higher ethyl levulinate “yields”, but do not affect the ethyl levulinate “yield” once steady-state has been achieved.
3. Higher feedstock loadings achieve lower ethyl levulinate “yields”.
4. Reaction time, reaction temperature, and feedstock loading appear to be dominant determinators of “yield”.
5. There appears to be no clearly discernible influence on the effectiveness of particular catalysts to achieve a greater actual steady-state yields. From Figure 13 (Chapter 2) of the five generic classes of catalyst, comparably high yields of 56, 61, 67 and 81 mol % are achieved with four different catalyst types, notably also dependent on reaction time and temperature. Reports of the performance of the zeolite catalyst class indicate they may produce a marginally higher yields of ethyl levulinate, but this is not at all conclusive.
6. With regard to feedstock identity. Yields obtained with actual biomasses are significantly lower than those achieved with glucose or cellulose. The higher yields are reported for corn cob (27 wt.%, this study), Mandarin peel (28 wt.%) and Cassava (31 and 36 wt.%). Given our understanding that the alkyl levulinates are principally produced from the cellulosic fraction of the biomass, these observations are plausible. It is important to note that nine of the thirteen studies on real biomasses, report yields much lower than 25 wt.%.

5.4.6 Ether Effect: Composition of Reaction Mixtures

Despite the surge of interest in the synthesis of alkyl levulinates from pure carbohydrates and lignocellulosic biomass, studies rarely determine the concentrations of the other main co-product, dialkyl ether, and the other feedstock, the alcohol [68, 70, 106, 108, 116, 134].

In literature studies, optimal yields of ethyl levulinate are targeted without consideration of the formation of major co-products, knowledge of which is essential to determining techno-economics. This trend tends to result in the studies configuring a lower feedstock concentration relative to the ethanol and acid concentrations so as to achieve maximum yields of ethyl levulinate. It is important to appreciate the difference between the yield of product (a ratio) and quantity of product (how much is produced in unit batch). Additionally, this practice has the unintended and undesirable effect of maximising the production of dialkyl ether. Surprisingly, the ether effect appears to be mostly overlooked in the literature.

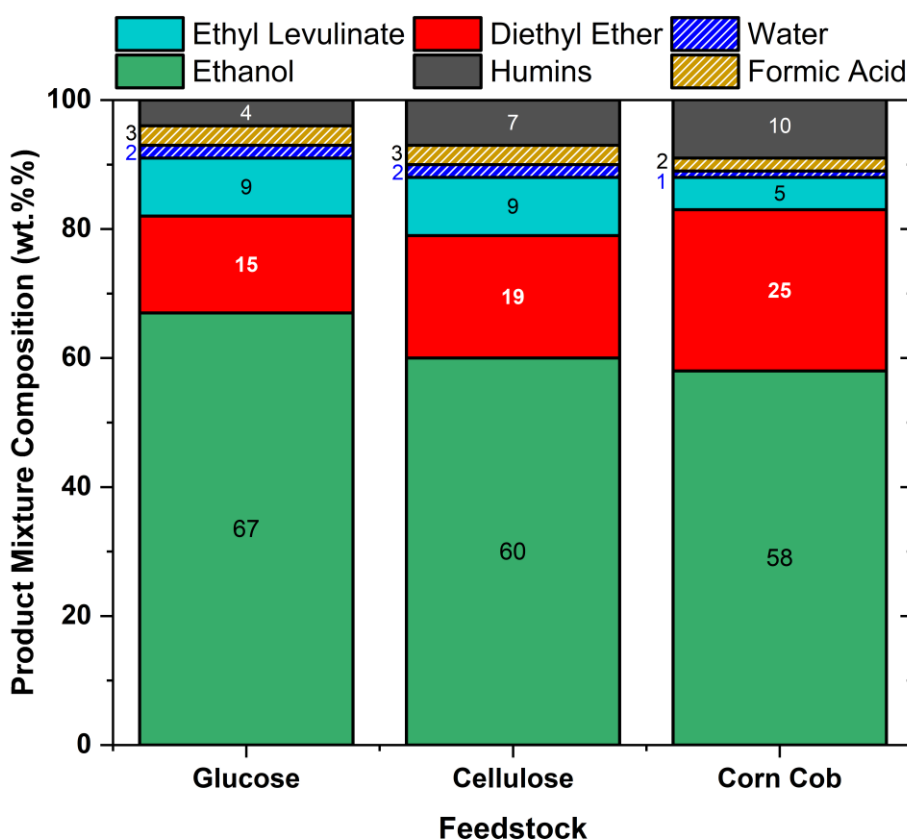


Figure 39. Composition of the reaction mixture (wt.%) at reaction conditions that give the highest ethyl levulinate to diethyl ether ratio normalised to 100 % based on the 6 main components of the reaction mixtures. The ethyl levulinate, diethyl ether, ethanol, and humins concentrations are experimentally measured. The water and formic acid concentrations are calculated stoichiometrically.

Figure 39 shows the product concentrations (wt.%) at the shortest time at which the steady-state of ethyl levulinate production has been reached, for 20 wt.% of feedstock (with 1 wt.% sulphuric acid for glucose and cellulose and 2 wt.% sulphuric acid for corn cob), as this produced the highest concentration of ethyl levulinate relative to diethyl ether out of the

three feedstock loadings. The concentrations of ethyl levulinate, diethyl ether, ethanol, and humins are experimentally determined, whereas the content of water and formic acid are modelled stoichiometrically from Equations 25-27.

For cellulose and glucose, Figure 39 shows that ethyl levulinate represents 9 wt.% of the reaction mixture for both feedstocks, with ether at 15 and 19 wt.%, respectively. Conversely, for the real-world biomass, corn cob, ethyl levulinate is 5 wt.%. Not surprisingly, the latter feedstock produced more diethyl ether as the amount of acid added is the highest. Therefore, to minimize the diethyl production while maximising ethyl levulinate formation, a minimum concentration of sulphuric acid should be used. Results show that this ideal feedstock:acid ratio falls in the range 10:1 – 20:1 at 150 °C for corn cob. From Figure 12 (Section 2.3.2), the catalyst concentrations typically employed in the literature are large, in the order of 0.5-15 wt.%. Given that the analysis of Figure 39 uses a lower concentration, 0.5-2% acid, it is reasonable to assume that the use of higher acid fractions would result in higher ether concentrations. Likewise, from Figure 39, the feedstock concentrations employed in this study are higher than that of most literature. This means that in available studies, ether formation is higher than what is depicted in Figure 39. Alcohol consumption and ether formation significantly affect the techno-economic viability of the process, which underscores the need for a fundamental knowledge of the ether effects.

5.4.7 Ethanolysis Surrogate Kinetic Model

Currently, the detailed reaction pathways and kinetics of the acid-catalysed ethanolysis of lignocellulosic biomass are not fundamentally known. The model is evaluated against the time-resolved experimental data to derive the empirical rate constants associated with each reaction in the model reaction network. Three consecutive optimisations of the glucose, cellulose, and corn cob sub-models against each set of feedstock experimental data resulted in the kinetic rate constants listed in Table 14.

Table 13. Coefficient of determination (R^2) for glucose, cellulose, and corn cob.

Feedstock	Ethyl Levulinate	Diethyl Ether	Ethanol
Glucose	0.97	0.94	0.97
Cellulose	0.97	0.94	0.97
Corn cob	0.87	0.95	0.97

The validity of the model in calculating the mass of ethyl levulinate and diethyl ether produced is assessed by the coefficient of determination value (R^2). For ethyl levulinate production from glucose, cellulose, and corn cob, R^2 values of 0.97, 0.97, and 0.87, were achieved respectively, and are displayed in Table 13. The difference in the rate of formation of ethyl levulinate between glucose and cellulose is reproduced by the model with the reaction rate constant of the depolymerisation reactions of cellulose, reactions 10 and 11. The corn cob surrogate model species, which consists of a non-interacting mixture of cellulose, hemicellulose, and lignin, only considers a reaction pathway to ethyl levulinate from cellulose. This simplified picture accurately predicted the yield reduction in the corn cob ethanolysis. The R^2 value of the model for diethyl ether production from glucose, cellulose, and corn cob are 0.94, 0.94, and 0.95, respectively. The mass of diethyl ether decreases with increasing mass loading. This is due to the lower initial mass of ethanol in the system and the “unknowns” formation through non-catalytic reactions. Notably, the model captures these effects. There is a higher rate of formation of diethyl ether in the glucose model, compared to that of cellulose, as a result of the acid consumption in the reaction of cellulose to “unknowns”. Under similar conditions, the mass of diethyl ether formed is significantly less for corn cob than for glucose and cellulose, which the model also replicates. In these reactions, hemicellulose and lignin react with a proton to produce “unknowns”, reducing the population of the latter and hindering the formation of diethyl ether.

Figure 32 summarises the elucidated kinetic model, which consists of 18 elementary steps. It should be emphasised that reactions 3-9 are optimised to all glucose data. Reactions 10-13 are optimised to cellulose data. Reactions 15-18 are optimised to corn cob data. The

composition of “unknown” variables is contingent upon the source species and the catalytic nature of the reaction under consideration.

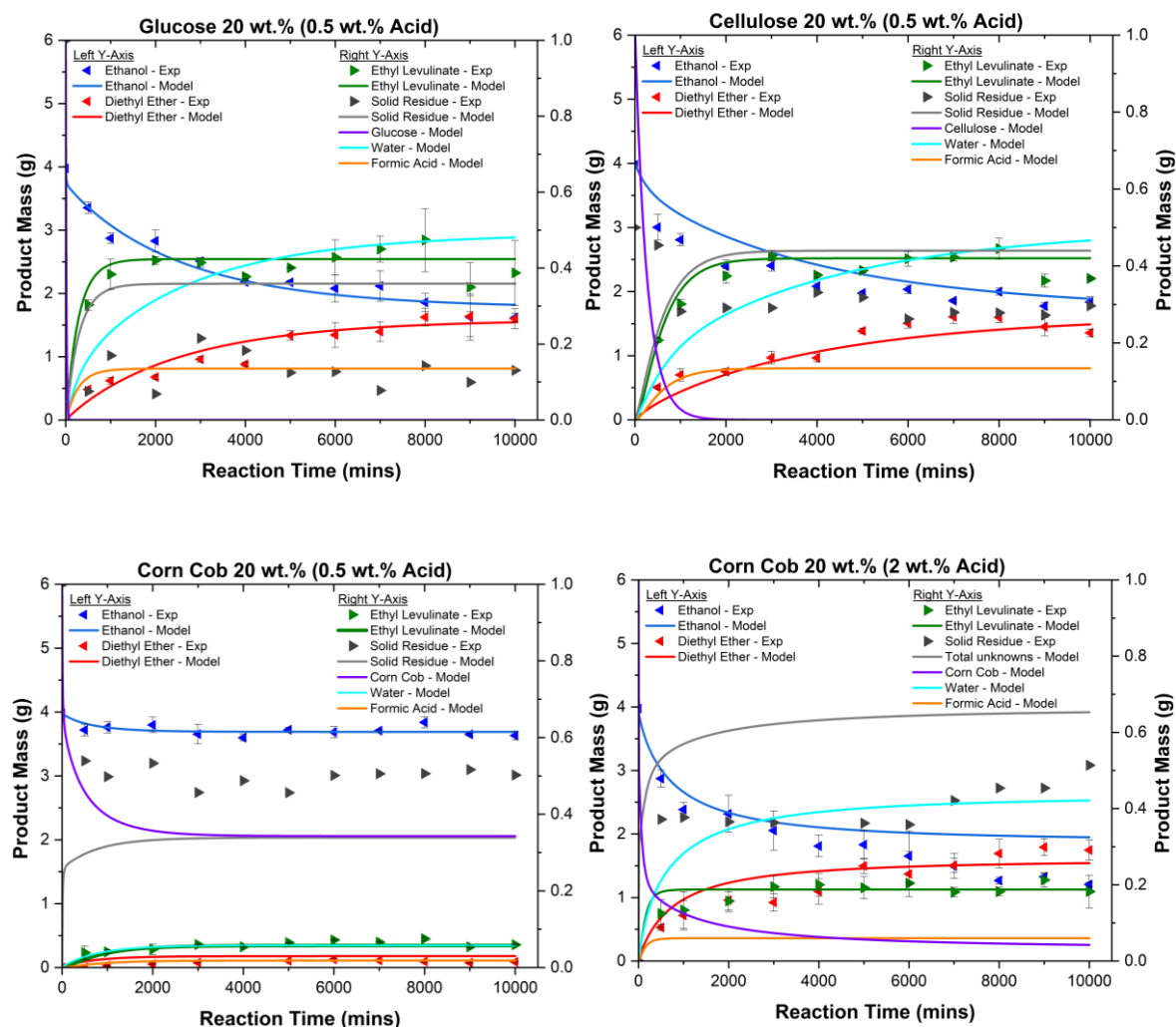


Figure 40. Product concentrations as a function of time for the acid-catalysed ethanolysis of glucose (20 wt.%, 0.5 wt.% H_2SO_4), cellulose (20 wt.%, 0.5 wt.% H_2SO_4), corn cob (20 wt.%, 0.5 wt.% H_2SO_4), and corn cob (20 wt.%, 2 wt.% H_2SO_4) at 150 °C. Each data point represents the average of four experimental replicates, with uncertainties corresponding to one standard deviation. Solid lines denote predictions from the surrogate kinetic model, where “Solid Residue – Model” is obtained by summing the masses of all species classified as “unknown” in Table 14 and Figure 32.

Figure 40 shows the species concentration as a function of time for the sulphuric acid-catalysed ethanolysis of glucose, cellulose, and corn cob (20 wt.%) at 150 °C as produced by the surrogate kinetic model. The model accurately predicts the relationship between these variables, overestimating, however, the mass of solid residue. This inconsistency might be related to the soluble species present in the reaction mixture as solid residue is calculated by summing the total unknowns, but this will contain both soluble and insoluble species. This may also be due to the mass loss of humins during centrifugation, which is highlighted in

Chapter 5. Ethanolysis

the elemental balance results section. Moreover, the effect of reactant concentration and the extent of hydrogen cation consumption on the relative concentrations of ethyl levulinate, diethyl ether, and ethanol are accurately reproduced by the model.

Notes for Table 14:

- Ethanol = C_2H_5OH
- Ethanol/ H^+ = $C_2H_5OH_2^+$
- Glucose = $C_6H_{12}O_6$
- Ethyl glucoside = $C_8H_{16}O_6$
- Cellulose = $(C_6H_{10}O_5)_n$
- Hemicellulose = $(C_5H_8O_4)_n$
- Lignin = $C_{10}H_{0.24}O_{0.64}N_{0.02}S_{0.01}$; Empirical composition inferred from ultimate analysis of corn cob, obtained by subtracting the contributions of cellulose and hemicellulose.
- Formic acid = $HCOOH$
- Ethyl levulinate = $C_7H_{12}O_3$
- Unknowns_{SpeciesX} = lumped products derived from species X, inferred by mass balance, and encompassing both solid and soluble

Table 14. Elucidated kinetic model. Rate constants, k, determined at 150 °C.

#	Reaction	k ($m^3 \text{ mol}^{-1} \text{ s}^{-1}$)
1	Ethanol + $H^+ \rightleftharpoons$ Ethanol/ H^+	2.34×10^{10}
2	$H_2O + H^+ \rightleftharpoons H_3O^+$	3.74×10^8
3	Ethanol + Ethanol/ $H^+ \rightleftharpoons$ Diethyl ether + H_3O^+	1.34×10^4
4	Glucose + Ethanol/ $H^+ \rightarrow$ Ethyl glucoside + H_3O^+	5.20×10^5
5	Ethyl glucoside + Ethanol/ $H^+ \rightarrow$ Ethyl levulinate + Formic acid + H_2O + Ethanol/ H^+	8.26×10^6
6	Glucose + $H^+ \rightarrow$ Unknowns_Glucose/ H^+ + $3.5H_2O$	2.37×10^5
7	Glucose + $H^+ \rightarrow$ Unknowns_Glucose + $3H_2O$ + H^+	1.03×10^1
8	Ethyl glucoside + $H^+ \rightarrow$ Unknowns_Ethylglucoside/ H^+ + $4.5H_2O$	5.45×10^{-1}
9	Ethyl glucoside + $H^+ \rightarrow$ Unknowns_Ethylglucoside + $4H_2O$ + H^+	1.19×10^2
10	Cellulose + $H_3O^+ \rightarrow$ Glucose + H^+	2.00×10^7
11	Cellulose + Ethanol/ $H^+ \rightarrow$ Ethyl glucoside + H^+	4.48×10^5
12	Cellulose + $H^+ \rightarrow$ Unknowns_Cellulose/ H^+ + $2.5H_2O$	8.84×10^0
13	Cellulose + $H^+ \rightarrow$ Unknowns_Cellulose/ H^+ + $2H_2O$ + H^+	2.57×10^1
14	Corn cob + $H^+ \rightarrow$ Cellulose + $0.882Hemicellulose$ + Lignin + H^+	1.00×10^{11}
15	Lignin + $H^+ \rightarrow$ Unknowns_Lignin + H^+	1.41×10^1
16	Lignin + $H^+ \rightarrow$ Unknowns_Lignin/ H^+	7.31×10^0
17	Hemicellulose + $H^+ \rightarrow$ Unknowns_Hemicellulose + H^+	9.98×10^2
18	Hemicellulose + $H^+ \rightarrow$ Unknowns_Hemicellulose/ H^+	7.11×10^3

5.4.8 Elemental Balance

An elemental balance is performed to aid in the techno-economic-analysis of the process. The moles of carbon, hydrogen, and oxygen in the products of this reaction (ethyl levulinate, diethyl ether, ethanol, humins, formic acid, and water) are quantified and expressed as a percentage of the moles of carbon, hydrogen, and oxygen present in both the feedstock and added ethanol. The concentrations of ethyl levulinate, diethyl ether, and ethanol are determined via gas chromatography. Two principal sources of potential mass loss are identified in the process: (i) loss of gases and (ii) humins loss during centrifugation. Both mechanisms are responsible for the trends observed in Figure 41. Mass loss is greatest in both the 5 and 20 wt.% of feedstock reactions.

For 5 wt.% of feedstock, there are higher ethanol and acid concentrations relative to feedstock. This favours the formation of diethyl ether and thus increases the pressure inside the reactor. Higher pressures resulted in a greater mass loss during the reaction. In contrast, for 20 wt.% of feedstock, a higher humins formation is observed, and thus the loss increases during centrifugation.

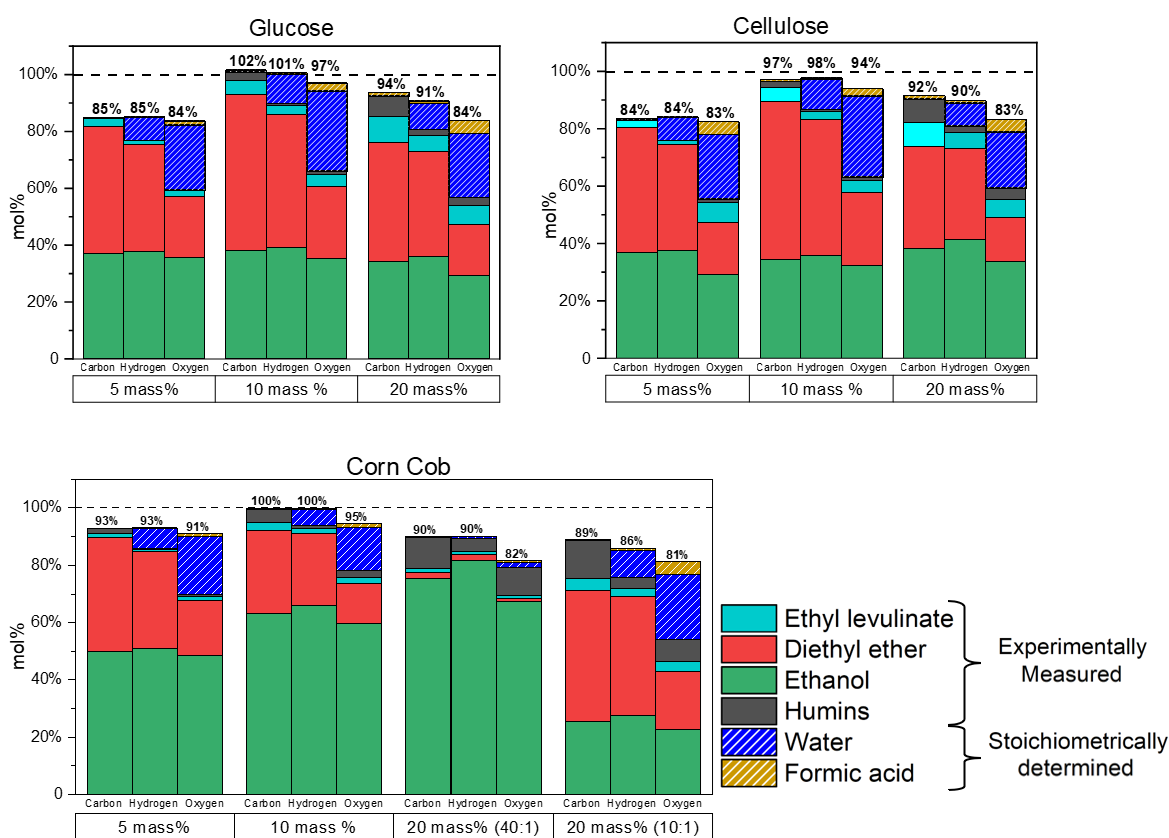


Figure 41. Mol% of carbon, hydrogen, and oxygen recovered at the end of 5, 10, 20 wt.% glucose, cellulose, and corn cob ethanolysis for 10000 minutes at 150 °C.

5.5 Conclusions of Ethanolysis Study

A self-consistent, hierarchical, and mass-conserved surrogate kinetic model that accurately replicates experimental results of the ethanolysis of glucose, cellulose, and corn cob is elucidated and validated. As a key novelty, the model employs the biochemical composition of the corn cob as a compositional surrogate, extending fundamental oriented kinetic modelling to actual biomasses, opening the door to allow kinetic models inform more comprehensive techno-economic-analyses of lignocellulose ethanolysis to produce advanced biofuels. To construct the model, a complete and high-quality experimental dataset for the steady-state conditions of ethyl levulinate production via sulphuric acid-catalysed ethanolysis at 150 °C for 5, 10, and 20 wt.% for each of glucose, cellulose, and corn cob, is established.

At all conditions, diethyl ether is observed as the major reaction co-product. Minimum diethyl ether concentrations relative to ethyl levulinate are achieved at the earliest steady-state times and the highest feedstock loading (20 wt.%), resulting in mass ratios of approximately 2:1, 2:1, and 5:1, for glucose, cellulose, and corn cob, respectively. The critical corn cob-to-acid mass ratio that minimizes the formation of undesired co-products (diethyl ether) ranged from 10–20:1 at 150 °C. The concentration of ethyl levulinate at steady-state, and the time needed to reach steady-state are specifically targeted as it is key information for techno-economic-analyses. The required time to reach the steady-state at 150 °C is found to be dependent on the relative complexity of each feedstock in the order of glucose (500-1000 minutes), cellulose (1000-2000 minutes), and corn cob (2000-3000 minutes). It is shown that the maximum average steady-state yields (wt.%) of ethyl levulinate from glucose, cellulose, and corn cob are respectively (46.6 ± 3.7), (50.2 ± 5.4) and (27.0 ± 1.9)% and are achieved at 5 wt.% feedstock, 0.5 wt.% sulphuric acid, and 94.5 wt.% ethanol.

Surprisingly, analysis shows that the yield of ethyl levulinate achieved from corn cob is higher than that predicted based on the cellulose content of the corn cob, and the experimentally determined ethyl levulinate yields from pure cellulose, therefore implying alternative sources of ethyl levulinate formation. This discovery indicates that ethyl levulinate may be formed by atypical conversions of the other biochemical constituents of corn cob, such as hemicellulose, directly challenging the common assumption that all ethyl levulinate produced from lignocellulosic biomass comes from its cellulose content alone.

Furthermore, as expected, the steady-state concentration of ethyl levulinate formed from glucose and cellulose is found to be independent of the acid concentration. Therefore, the conversion of glucose and cellulose to ethyl levulinate in the presence of ethanol and sulphuric acid is concluded to be truly catalytic in nature. Conversely, in the case of corn cob, the steady-state concentration of ethyl levulinate is shown to be highly dependent on the acid concentration until a maximum quantity of ethyl levulinate is achieved. The observations presented are consistent with a basic hypothesis that the hydrogen cations originating from the acid catalyst are consumed in some irreversible process. This is further evidenced by the negligible quantities of diethyl ether observed for experiments using the highest corn cob-to-acid mass ratio (40:1), indicating that the alcoholysis of lignocellulosic biomass is not wholly a catalytic process

The findings of this ethanolysis study establish a mechanistic and kinetic framework for understanding lignocellulosic alcoholysis. By confirming the catalytic behaviour of glucose and cellulose, identifying the acid-dependence of corn cob, and demonstrating direct contributions from hemicellulose, the work highlights both the opportunities and limitations of ethanol as a solvent. These insights provide the basis for extending the surrogate kinetic modelling framework to butanolysis, where differences in solvent structure, reactivity, and product distribution further test the generality of the approach and its implications for advanced biofuel production.

Chapter 6

Butanolysis

6.1 Introduction

6.1.1 Context and Significance of Butanolysis in Advanced Biofuels

The transport sector, covering road, aviation, and maritime modes, remains heavily dependent on fossil fuels and is a major source of anthropogenic CO₂ emissions, which drive global climate change [217]. Reducing the carbon intensity of transport fuels is therefore essential to meet climate and energy targets. Advanced biofuels, as defined in the Renewable Energy Directive, are central to this transition, as they are derived from non-food feedstocks such as agricultural and forestry residues and other designated wastes [27]. Lignocellulosic biomass is particularly attractive because it is abundant, low cost, and underutilised, yet its inherent recalcitrance and high oxygen content present significant challenges for conversion into energy-dense liquid fuels [226].

A wide range of thermochemical and catalytic conversion technologies has been investigated for lignocellulosic valorisation, including hydrolysis [220], alcoholysis [66], pyrolysis [221], gasification [222], hydrothermal liquefaction [223] and hydrothermal carbonisation [224]. Among these, alcoholysis, acid-catalysed hydrolysis in an alcohol medium, offers distinct advantages, as it simultaneously depolymerises carbohydrates and esterifies reactive intermediates, producing alkyl levulinates and dialkyl ethers in a single step [39]. These compounds are versatile: alkyl levulinates are promising fuel additives and solvents [35], while dialkyl ethers serve as high-cetane blending components [227]. The alcohol itself, if renewable, further enhances process sustainability.

Ethanolysis has historically received the greatest research attention, but butanolysis has emerged as a strategically superior pathway [40]. When conducted in *n*-butanol, the process yields mixtures of *n*-butyl levulinate, di-*n*-butyl ether, and unreacted *n*-butanol. These blends exhibit higher energy density, lower hygroscopicity, and improved miscibility with diesel compared with their ethyl analogues [41]. Moreover, *n*-butanol can be produced from renewable microbial fermentation routes, such as *Clostridium acetobutylicum* [228], supporting the transition to a fully biobased fuel cycle.

From a green chemistry perspective, alcoholysis exemplifies the principles of catalysis, atom economy, and renewable feedstock utilisation [119]. Its co-production of levulinates, ethers, and residual alcohol aligns with circular economy goals by maximising resource efficiency. Furthermore, the previous modelling efforts in ethanolysis (Chapter 5) have demonstrated the potential of surrogate-based kinetic frameworks to predict yields across biomass feedstocks [124], suggesting that similar approaches can be extended to butanolysis to guide optimisation and scale-up. Taken together, these features position butanolysis as a particularly significant pathway within the portfolio of advanced biofuel technologies.

6.1.2 Research Gap and Rationale for Butanolysis

Although ethanolysis has been more extensively studied, recent work demonstrates that butanolysis yields biofuel intermediates with superior physical and combustion properties. In particular, the key products, *n*-butyl levulinate, di-*n*-butyl ether, and unreacted *n*-butanol, form blends that outperform their ethyl counterparts in several critical respects. Wiseman and co-workers showed that butyl-based ternary blends are stable when blended with diesel up to 25 vol%, whereas ethyl-based blends suffered instability at equivalent levels due to high diethyl ether content [40]. Engine tests further revealed that butyl blends maintained stable combustion across load conditions, exhibited negligible changes in brake-specific fuel consumption (BSFC), and preserved mechanical efficiency, while ethyl blends showed unstable operation and elevated BSFC. Importantly, butyl blends reduced particulate matter (PM_{2.5}) and particle number (PN) emissions compared with diesel, without penalising NO_x emissions, thereby offering tangible air quality benefits [40].

These advantages arise from the intrinsic properties of butyl derivatives: higher energy density, lower hygroscopicity, and superior miscibility with diesel compared to ethyl

analogues [41]. Consequently, butanolysis is increasingly recognised as a strategically advantageous pathway for producing advanced biofuels with greater compatibility to existing fuel standards and infrastructure.

Despite this potential, the butanolysis literature remains sparse and fragmented relative to ethanolysis. Most reports have focused on catalyst screening with glucose or cellulose as model substrates, with comparatively few studies addressing real lignocellulosic feedstocks [66]. Figure 42 summarises the available one-pot butanolysis studies, expressed in terms of mass yield for comparability. The limited number of data points highlights how little systematic work has been performed, and how reporting inconsistencies continue to hinder fair cross-study comparison. Conventional yield practices, typically normalised solely to cellulose, systematically overestimate molar yields and overlook hemicellulose-derived contributions such as alkyl levulinate formation from xylan [124].

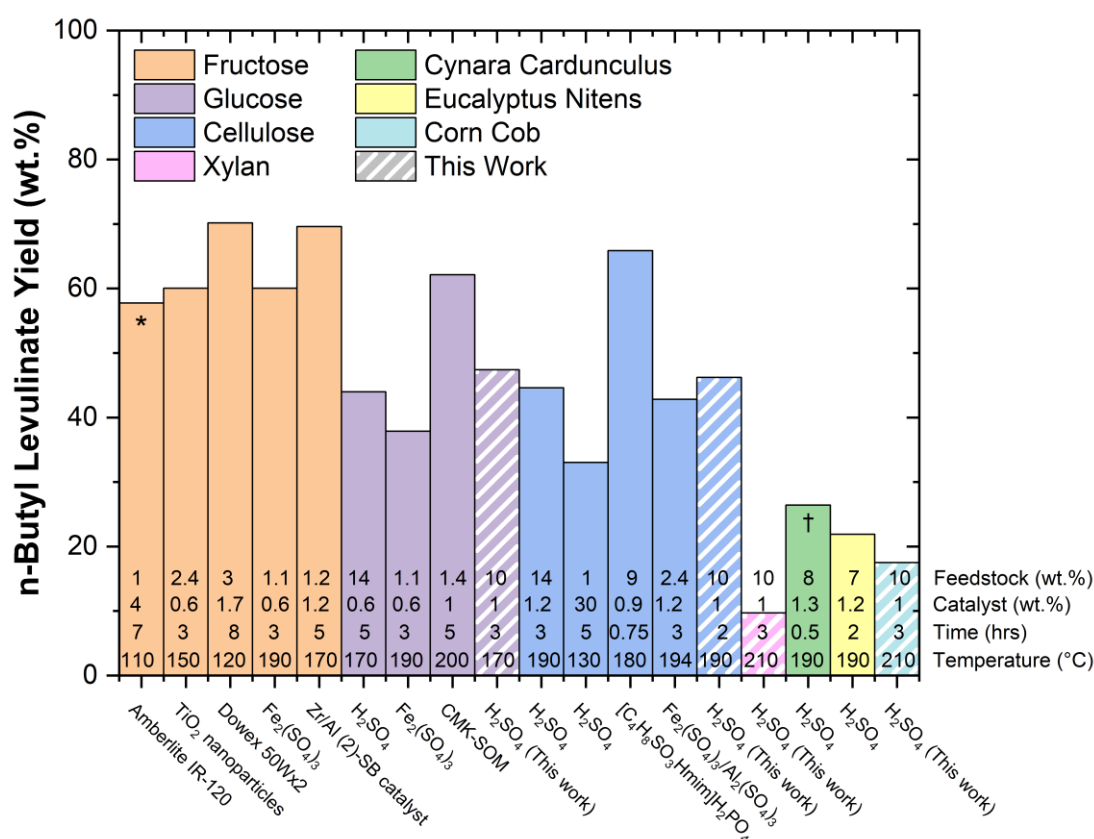


Figure 42. Mass yields of n-butyl levulinate obtained from various feedstocks [36, 120, 121, 143-151]. Yields are expressed according to Equation 38. Each data point represents a one-pot system containing only butanol, catalyst, and feedstock, with the striped columns indicating this work. The asterisk (*) indicates the use of a co-solvent system comprising γ -valerolactone (GVL) and butanol (30/70 wt%). (†) Indicates that microwave-assisted heating and steam explosion pretreatment were employed.

In summary, although butyl-based fuels clearly offer superior performance potential, systematic studies of butanolysis remain limited, and current yield methodologies misrepresent process efficiency. These knowledge gaps provide the rationale for the present investigation.

6.2 Objectives

The objectives of this chapter were fivefold:

1. To define steady-state as the benchmark for butanolysis, and to quantify steady-state yields and times for glucose, cellulose, xylan, and corn cob across 170–210 °C under sulphuric acid catalysis.
2. To measure complete product distributions at steady-state, explicitly quantifying n-butyl levulinate, di-n-butyl ether, n-butanol, water, formic acid, and humins, and to close carbon and alcohol balances for process assessment.
3. To establish a rigorous yield framework that corrects cellulose-only normalisation by incorporating cellulose and hemicellulose in molar yields, alongside mass yield, carbon yield, and space time yield for comparability and techno-economic and life-cycle assessments.
4. To determine the effects of temperature, acid dosage, and reaction time on selectivity, identifying operating windows that maximise n-butyl levulinate while limiting ether formation and water generation.
5. To extend and validate a hierarchical surrogate kinetic model for butanolysis, reproducing concentration–time profiles, embedding experimentally derived activation energies, and enabling prediction of yields and space time yields for process design and feedstock screening.

In pursuing these objectives, unanticipated findings prompted further analyses that revealed additional mechanistic features of acetyl chemistry and furfural-driven humin formation. While not envisaged at the outset, these insights deepened the interpretation of results and broadened the scope of the conclusions.

6.3 Methodological Critique of Yield Representation

A central challenge in evaluating alcoholysis lies not only in the diversity of reported feedstocks and catalysts but also in the inconsistent approaches used to quantify yield. In much of the alcoholysis literature, yields are reported in molar terms normalised solely to the cellulose fraction of biomass, implicitly assuming that alkyl levulinates originate only from cellulose [120, 121]. While this simplification is convenient, it systematically overestimates molecular efficiency and obscures the contributions of other fractions.

Chapter 5 demonstrated that hemicellulose, particularly in the form of xylan, is also a precursor to alkyl levulinate formation under one-pot alcoholysis conditions. Neglecting this contribution misrepresents the overall carbon economy and undermines comparability across feedstocks of differing biochemical composition. This issue extends beyond butanolysis to ethanolysis and hydrolysis studies [112, 229-231]. Consequently, conventional yield reporting distorts process efficiency and hampers techno-economic analysis and life-cycle assessment.

To address this gap, the present thesis employs a revised framework for yield calculation that explicitly incorporates both cellulose- and hemicellulose-derived contributions. By aligning yield metrics more closely with the biochemical basis of lignocellulosic biomass, this approach improves consistency, enables cross-study comparison, and provides a more realistic assessment of process performance. The following subsections briefly restate the relevant yield definitions, now applied directly to the butanolysis of model carbohydrates and lignocellulosic feedstocks, to guide interpretation of the results that follow.

6.3.1 Mass Yield

Mass yield expresses the proportion of biomass converted to butyl levulinate (BL), calculated as a weight percentage relative to the initial feedstock.

$$Yield \text{ (wt. \%)} = \frac{\text{Butyl levulinate (g)}}{\text{Biomass (g)}} \times 100 \quad (38)$$

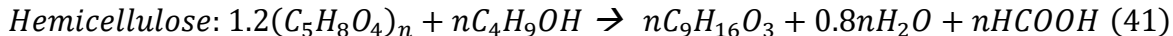
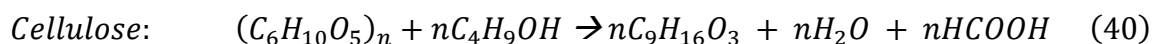
This metric is simple and widely reported [44], making it useful for benchmarking across diverse feedstocks. However, it does not reflect molecular efficiency or account for the

contribution of butanol to the overall process. Figure 42 presents these literature yields alongside results from this work, highlighting both the variability in reported values and the value of a harmonised reporting basis. The striped columns denote experiments performed in this study, while symbols indicate cases where co-solvents, microwave heating, or pretreatment were applied.

6.3.2 Molar Yield (Cellulose + Hemicellulose)

Molar yield quantifies the efficiency of butyl levulinate formation relative to the maximum theoretical yield from both cellulose and hemicellulose.

$$\text{Yield (mol\%)} = \frac{\text{Butyl levulinate (mol)}}{\text{Max. yield from cellulose and hemicellulose (mol)}} \times 100 \quad (39)$$



By including hemicellulose-derived contributions, this approach corrects the limitations of cellulose-only methods commonly found in the literature [35, 87, 198]. It provides a rigorous framework for comparing results across feedstocks, although its application to real biomass requires simplifying assumptions about polymeric composition.

6.3.3 Carbon Yield

Carbon yield measures how effectively carbon from the feedstock is incorporated into butyl levulinate (BL), accounting for the fact that five carbons derive from the carbohydrate fraction and four from butanol.

$$\text{Carbon Yield (mol\%)} = \frac{\text{Moles of C formed as BL}}{\text{Max moles of C converted to BL}} = \frac{BL (g) \times C \text{ in BL (wt.\%)}}{\left(\frac{9}{5}\right) \times \text{Feedstock (g)} \times C \text{ in Feedstock (wt.\%)}} \quad (42)$$

The 9/5 term accounts for the mechanistic fact that five of the nine carbon atoms in *n*-butyl levulinate come from the reacted carbohydrate, while the remaining four come from *n*-butanol [35].

This metric is particularly valuable for tracing carbon allocation between butyl levulinate, humins, and other by-products, and for linking experimental results with carbon balances in life-cycle assessment studies [158, 232]. While less intuitive than mass or molar yields, it provides unique insights into atom efficiency.

6.3.4 Space-Time Yield

Space-time yield reflects reactor productivity, expressed as the mass of BL produced per unit reactor volume per unit time.

$$STY \text{ (g}L^{-1}h^{-1}\text{)} = \frac{\text{Butyl levulinate at } T_{90} \text{ (g)}}{\text{Reactor volume (L)} \times T_{90} \text{ (h)}} \quad (43)$$

Unlike percentage yields, space-time yield highlights process intensification and scale-up potential, making it a key parameter for techno-economic assessments [233-235]. In this study, space-time yield was calculated based on T_{90} , the time required to reach 90% of the predicted maximum yield (to be consistent with our definition of steady-state), allowing comparison across conditions despite the non-optimised reactor configuration.

6.4 Methodologies Employed

The butanolysis experiments presented in this chapter were conducted using Alcoholysis Procedure – Method B (Section 3.3.2), developed to permit higher-temperature operation than Method A. Feedstock, *n*-butanol, and sulphuric acid were combined in PTFE liners inside sealed stainless-steel autoclaves (total mass 5 g) and heated at 170–210 °C for the specified reaction time. After cooling, the mixtures were centrifuged, neutralised with sodium hydrogen carbonate (50 mg), and diluted in dimethyl sulfoxide (400:1 solvent-to-sample ratio) prior to gas chromatography analysis. Product yields were quantified by GC-FID as described in Section 3.4.1. All experiments were performed in duplicate with

analytical replicates, giving four data points per condition; uncertainties are reported as one standard deviation

As in the ethanolysis study, steady-state was explicitly defined as the earliest time at which product yields no longer varied within experimental uncertainty, ensuring that reported yields of butyl levulinate and dibutyl ether reflected maximum attainable values.

Kinetic modelling employed the Butanolysis Surrogate Kinetic Model Mechanism (Section 3.7.3.2), an extension of the ethanolysis framework with additional reactions to account for the inclusion of the xylan submodel as well as the mechanisms of formation of the additional products identified. Submodels were developed for glucose, cellulose, xylan, and corn cob, parameterised using compositional data from Chapter 4. The extended mechanism provided a more detailed representation of ester, ether, and by-product pathways, enabling predictive interpretation of the experimental steady-state data obtained under Method B conditions.

6.5 Results and Discussion

6.5.1 Reaction Conditions

The butanolysis study was initiated by adopting conditions previously optimised for ethanolysis (Figure 43), where feedstock loadings of up to 20 wt.% had delivered sufficiently high yields. The choice of *n*-butanol was informed by experimental studies comparing butanol isomers that show *n*-butanol consistently affords higher levulinate yields than secondary or tertiary isomers, with tertiary alcohols in particular leading primarily to alcohol dehydration and negligible ester production. The superior reactivity of primary alcohols is attributed to their reduced steric hindrance and greater tendency to form reactive alkoxides under acidic conditions, which favour levulinate formation [236]. For these reasons, *n*-butanol was selected as the representative isomer for the present butanolysis experiments.

At this 20 wt.% feedstock loading, glucose performed similarly under both ethanol and *n*-butanol, giving *n*-butyl levulinate yields of approximately 40.4 wt.%, identical to the ethanolysis benchmark. Cellulose also behaved comparably, with butanolysis achieving 35.8

wt.% compared with 38.9 wt.% in ethanolysis, although the product mixtures became highly viscous beyond five hours at 170 °C, limiting operability.

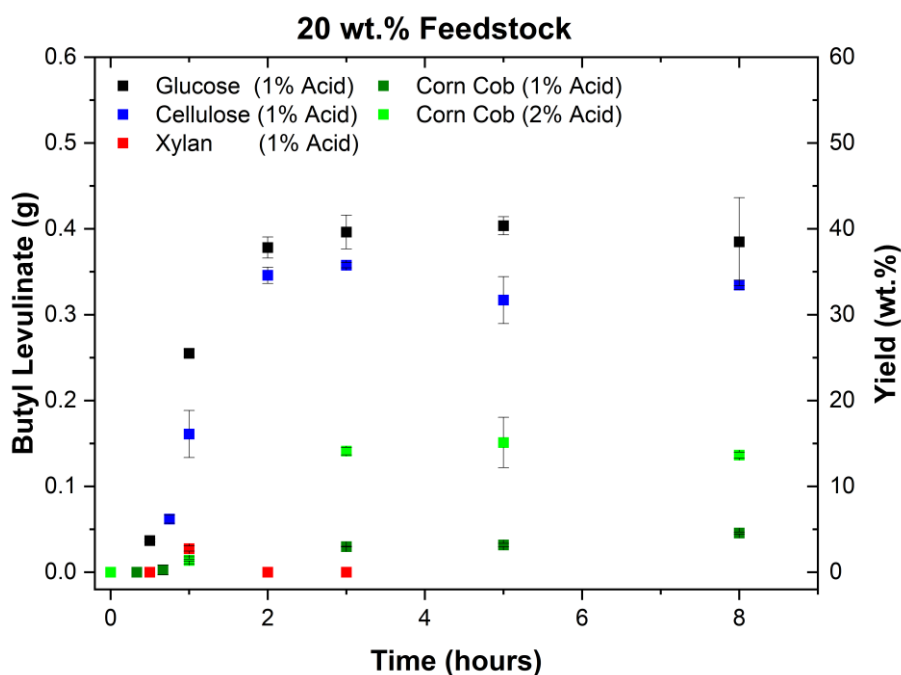


Figure 43. Yields of n-butyl levulinate (g, left axis; wt.%, right axis) as a function of reaction time for glucose, cellulose, xylan, and corn cob at 170 °C under varying acid loadings.

In contrast, xylan at 20 wt.% displayed markedly different behaviour. After only three hours at 170 °C, the reaction mixture had fully solidified, leaving no supernatant for analysis (Figure 44). This phenomenon is attributed to the rapid formation of furfural from xylan monomers, followed by its acid-catalysed polymerisation into insoluble humins. Such behaviour is well documented in related systems [196, 237, 238] and provides a compelling explanation for the disproportionate humin yields associated with hemicellulosic feedstocks. To mitigate this effect and enable accurate product quantification, all subsequent



Figure 44. Solidification of the xylan reaction mixture during acid-catalysed butanolysis at 20 wt.% loading after 3 h at 170 °C.

experiments were performed at 10 wt.% feedstock loading. This adjustment minimised viscosity and solidification issues, while ensuring consistent comparison across glucose, cellulose, xylan, and lignocellulosic biomass feedstocks.

Corn cob required further modification relative to ethanolysis. At 1 wt.% H₂SO₄, yields of *n*-butyl levulinate were stunted, whereas doubling the catalyst concentration to 2 wt.% increased yields to a maximum of 15.1 wt.% (Figure 43). A feedstock-to-acid ratio of 10:1 was therefore adopted for all subsequent corn cob experiments. As a consequence of these deviations from the standardised conditions, the surrogate kinetic model was not trained to this experimental dataset, and no model-predicted lines are shown alongside the results.

6.5.2 Steady-State Yields of *n*-Butyl Levulinate

Table 15 summarises the maximum mass, molar, and carbon yields obtained from the conversion of various feedstocks (10 wt.%) to *n*-butyl levulinate using a sulphuric acid catalyst (1 wt.%) in an *n*-butanol solvent (89 wt.%). Figure 45 shows the corresponding concentration profiles of *n*-butyl levulinate across reaction times of 0.5–5 h at 170, 190, and 210 °C, from which the maximum yields in Table 15 were determined.

Table 15. *n*-Butyl levulinate optimal yields, reaction conditions, and steady-state reaction times.

Feedstock	Temperature (°C)	Max. time to reach steady-state (hrs)	Max. yield reaction time (hrs)	<i>n</i> -Butyl Levulinate Yields		
				Wt. %	Molar %	Carbon %
Glucose	170	2	3	47.4	49.6	41.3
	190	2	4	45.9	48.0	40.0
	210	0.5	3	40.5	42.5	35.3
Cellulose	170	3	3	44.4	41.8	36.9
	190	2	4	46.2	43.4	38.3
	210	1	2	39.0	36.7	32.4
Xylan	170	2	3	7.7	7.0	6.5
	190	2	3	8.2	7.6	7.0
	210	1	3	9.7	8.9	8.3
Corn cob	170	3	3	15.7	25.8	12.6
	190	3	4	17.2	28.4	13.9
	210	2	3	17.5	28.8	14.1

6.5.2.1 *n*-Butyl levulinate mass yields

Mass yields of *n*-butyl levulinate were highest for glucose and cellulose across all conditions, with optimal values observed at temperatures ranging from 170 to 190 °C. Glucose achieved a maximum mass yield of $(47.4 \pm 2.7)\%$ at 170 °C, followed by a slight decline to $(45.9 \pm 1.1)\%$ at 190 °C and further to $(40.5 \pm 0.9)\%$ at 210 °C. Similarly, cellulose showed comparable performance, peaking at $(46.2 \pm 0.7)\%$ at 190 °C before decreasing to $(39.0 \pm 4.8)\%$ at 210 °C. As glucose and cellulose are simpler structures, the increase in the reaction temperature favours the formation of additional side products, such as humins.

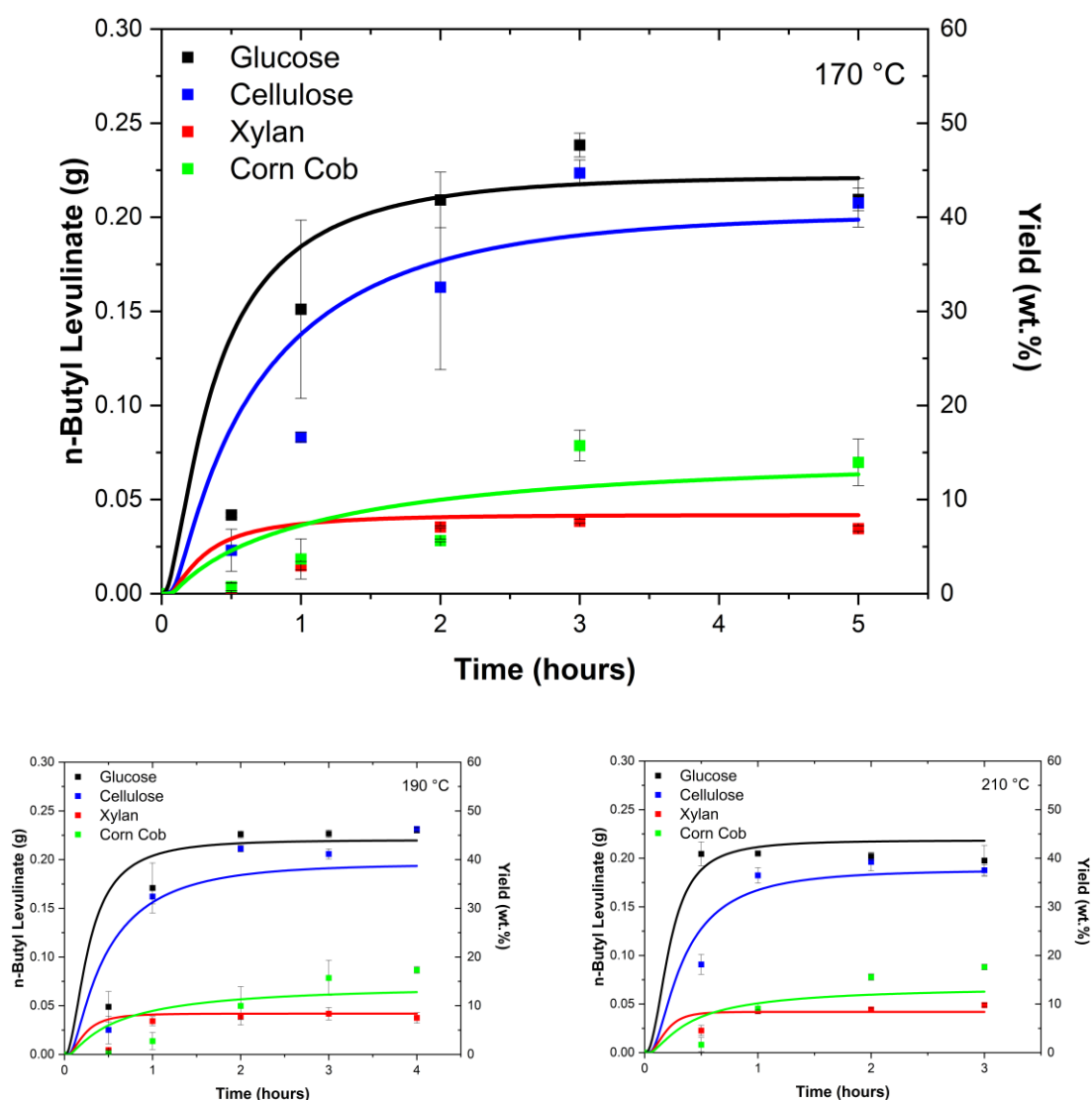


Figure 45. *n*-Butyl levulinate (g) produced by acid-catalysed butanolysis of glucose, cellulose, xylan and corn cob at 170, 190, and 210 °C for various reaction times. The square symbols represent experimental data points while the lines were produced by the surrogate kinetic model. The uncertainties represent the standard deviation of the four data points collected for each set of experimental conditions.

For corn cob, the maximum mass yield of $(17.5 \pm 3.1)\%$ was attained at 210 °C. In a novel finding, *n*-butyl levulinate was also formed from xylan, demonstrating that levulinate formation occurs from both the cellulose and hemicellulose constituents of the biomass. Although xylan achieved comparatively lower yields of *n*-butyl levulinate: $(9.7 \pm 3.7)\%$ at 210 °C, hemicellulose must now also be included in molar yield calculations. The more complex feedstocks, xylan and corn cob, achieved their highest yields at 210 °C, underscoring the recalcitrance of lignocellulose and demonstrating that higher temperatures promote the cleavage of carbohydrates and sugars from the lignocellulosic matrix. As mentioned, the presence of lignin in the corn cob represents the recalcitrance in the acid-catalysed butanolysis, indicating that higher temperatures are required for the H^+ to penetrate inside the plant cell. However, higher temperatures also favour the formation of di-*n*-butyl ether and other side reactions (many of which result from dehydration reactions), posing a trade-off that may hinder the commercial feasibility of one-pot alcoholysis processes.

6.5.2.2 *n*-Butyl Levulinate Molar Yields

Molar yields followed a similar pattern to mass yields. Glucose reached a peak molar yield of $(49.6 \pm 2.7)\%$ at 170 °C, whereas cellulose peaked at $(43.4 \pm 0.7)\%$ at 190 °C. For corn cob and xylan, the highest molar yields (28.8 ± 3.1) and $(8.9 \pm 3.7)\%$, respectively, were observed at 210 °C. For corn cob, this peak reflects the molecular efficiency of the process. Conversely, the discrepancy between mass-based and mole-based yields is because molar yield considers only the fractions of the biomass (cellulose and hemicellulose) that directly contribute to *n*-butyl levulinate production, as mentioned in Section 6.3.2.

Previous investigations on hydrolysis, ethanolysis, and butanolysis, report molar yield considering only the cellulose contribution to *n*-butyl levulinate [106, 120, 121], artificially inflating the yield and obscuring the actual molecular efficiency of such processes. This work proposes that molar yield should always be reported in accordance with the methods outlined in Section 6.3.

6.5.2.3 *n*-Butyl Levulinate Carbon Yields

Carbon yields, which measure the proportion of biomass-derived carbon contributing to *n*-butyl levulinate formation, showed trends analogous to the mass and molar yields. Glucose and cellulose achieved the highest carbon yields of 41.3% and 38.3% at 170 °C and 190 °C, respectively. Corn cob achieved a maximum carbon yield of 14.1% at 210 °C, while xylan reached its optimal carbon conversion of 8.9% at the same temperature.

These results demonstrate that, under optimised conditions, a substantial proportion of feedstock carbon can be successfully directed toward *n*-butyl levulinate production, particularly from glucose and cellulose. However, lower carbon yields to *n*-butyl levulinate indicate significant carbon losses to side products or insoluble residues for lignocellulosic substrates such as corn cob and xylan. To better account for the fate of feedstock carbon and assess overall process efficiency, the carbon molar yields of the humins formed are reported and discussed in Section 6.3.3.

6.5.2.4 Temperature Effect and Feedstock-Specific Observations

Optimal yields for glucose and cellulose occurred at 170–190 °C, reflecting their simpler structures and lower energy requirements for depolymerisation and conversion. However, yields for these feedstocks declined at 210 °C, likely due to decomposition of the product or the formation of other liquid by-products. In contrast, corn cob and xylan required higher temperatures (190–210 °C) to reach their peak yields. For corn cob, this is attributed to its more complex chemical composition and recalcitrance, particularly associated with the lignin fraction bound within the lignocellulosic matrix, demanding more thermal energy to break down into reactive intermediates.

Despite the superior performance of higher-temperature configurations in producing *n*-butyl levulinate from lignocellulosic biomass, more moderate reaction temperatures offer a clear advantage in minimising side reactions. One significant side reaction is the formation of di-*n*-butyl ether, which not only consumes the costly alcohol (a costly reagent which on average accounts for 38% of the cost of the process [37]) but also generates water, complicating downstream processing. Suppressing this undesired reaction is therefore a key objective of this study and can be achieved by reducing both the acid concentration and the reaction temperature.

Among all the temperatures tested, 190 °C emerged as the optimal condition, for 10 wt.% feedstock and 1 wt.% H₂SO₄, striking a balance between achieving high *n*-butyl levulinate yields and limiting ether formation. This temperature facilitated effective conversion across a range of biomass feedstocks of different complexity, including more recalcitrant materials, while mitigating the extent of etherification. As such, 190 °C represents a compromise that enhances overall process selectivity and economic efficiency.

6.5.2.5 Steady-State Conditions

In this study, the steady-state reaction time is defined as the shortest duration at which the mass of *n*-butyl levulinate remains constant (within ± 10 % experimental uncertainty) over three consecutive hourly samples. As reported in Section 6.5.2.4, 190 °C was identified as the optimum temperature for maximising *n*-butyl levulinate yields across all four feedstocks examined. At this temperature, glucose, cellulose, and xylan attained a steady-state within 2 hours, whereas the more recalcitrant corn cob feedstock required 3 hours.

Steady-state times lengthen as feedstock complexity increases (glucose < cellulose < xylan < corn cob) and increase further at lower temperatures owing to slower kinetics. Notably, the side-reaction forming di-*n*-butyl ether does not reach equilibrium under any of the conditions tested. Therefore, reaction durations should be carefully limited to minimise ether formation. While maximum *n*-butyl levulinate yields do not always coincide with the earliest steady-state time points, the highest levulinate-to-ether ratios are consistently observed at these earlier stages. This finding underscores the importance of accurately defining steady-state conditions when performing techno-economic and life-cycle assessments for potential commercial applications. Overall, the results highlight the critical interplay between feedstock reactivity, temperature, and reaction time in optimising process efficiency and product selectivity.

6.5.3 The Ether Effect

The formation of di-*n*-butyl ether is a significant side reaction in acid-catalysed butanolysis, arising from the dehydration of two *n*-butanol molecules in the presence of an acid catalyst, as described by Equation 28. The phenomenon parallels diethyl ether

production in ethanolysis reactions and can substantially influence process optimisation and techno-economic viability as it consumes the costly alcohol and produces water. In this way, a derivative molecule is generated, making the entire process less environmentally sustainable. Although it has been shown that blends of the alkyl levulinate, alcohol, and dialkyl ether can enhance fuel properties relative to any individual component [41, 122], these mixtures often contain comparatively small concentrations of the dialkyl ether. Thus, its formation should be minimised for commercial processes.

Figure 46 shows the concentrations of di-*n*-butyl ether produced from the feedstocks at two hours over the three temperatures. In many studies, efforts focus on maximising *n*-butyl levulinate yield, with comparatively little attention paid to the accumulation of di-*n*-butyl ether [148]. Although high di-*n*-butyl ether concentrations can increase downstream separation costs, reducing *n*-butanol availability for *n*-butyl levulinate production and diminishing overall process efficiency, this variable has been frequently overlooked [121]. Consequently, we have integrated this quantity into our analysis, which involves measuring di-*n*-butyl ether concentrations over time using gas chromatography (GC) and confirming the results via mass spectrometry (MS). This approach reveals that di-*n*-butyl ether formation tends to accelerate under conditions of elevated temperature, higher acid loading, and extended reaction times.

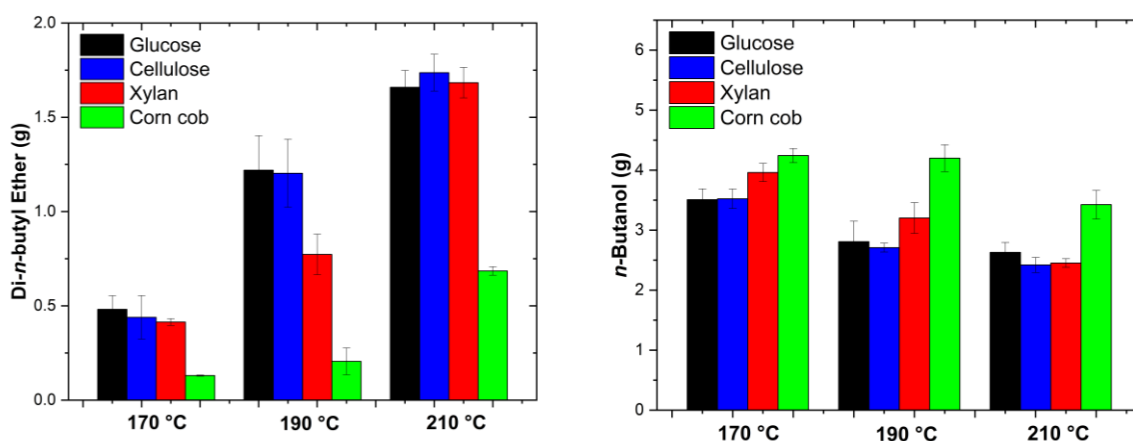


Figure 46. Mass of di-*n*-butyl ether (g) and *n*-butanol (g) produced via the sulphuric acid catalysed butanolysis of glucose, cellulose, xylan, corn cob, and wheat straw at 170, 190, and 210 °C for a reaction time of 2 hrs. The uncertainties represent the standard deviation of the four data points collected for each set of experimental conditions.

In terms of techno-economics, targeting the maximum *n*-butyl levulinate yield alone may be suboptimal. Instead, reaction severity, encompassing temperature, acid concentration, and

reaction duration, must be carefully balanced to moderate di-*n*-butyl ether formation while still achieving commercially relevant *n*-butyl levulinate outputs. A detailed understanding of the relative rates of *n*-butyl levulinate and di-*n*-butyl ether formation is crucial to devising efficient, cost-effective butanolysis processes at an industrial scale. Thus, the optimal reaction times achieved are the shortest at which steady-state of *n*-butyl levulinate production is observed and are reported in Table 15.

6.5.4 Major Species Fractions

Figure 47 presents the concentrations of both major and minor species detected during the sulphuric acid-catalysed butanolysis of glucose, cellulose, xylan, and corn cob. All products were quantified using gas chromatography and their identities confirmed by mass spectrometry techniques.

n-Butanol and di-*n*-butyl ether

The primary compounds detected in all feedstock reactions were *n*-butanol and di-*n*-butyl ether, with the latter (formed as described by reactions 3f and 3r in Table 19) emerging as the most abundant by-product for most conditions. Because both compounds are present in significant quantities, they dominate the overall mass balance for the mixtures.

n-Butyl levulinate

n-Butyl levulinate was observed in all reaction mixtures, confirming that levulinates can form from a wide range of biomass-derived substrates. To the authors' knowledge, this is the first study reporting the formation of *n*-butyl levulinate from xylan using a one-pot process. Notably, this unveils that levulinates can be produced from hemicellulose at relatively high yields (9.7 wt.% or 8.9 mol%). As discussed in Section 6.3, all molar yields in this paper were calculated based on the sum of monomeric units in both the cellulose and hemicellulose fractions of the biomass, accounting for the newly confirmed pathway (as described in Equations 40 and 41).

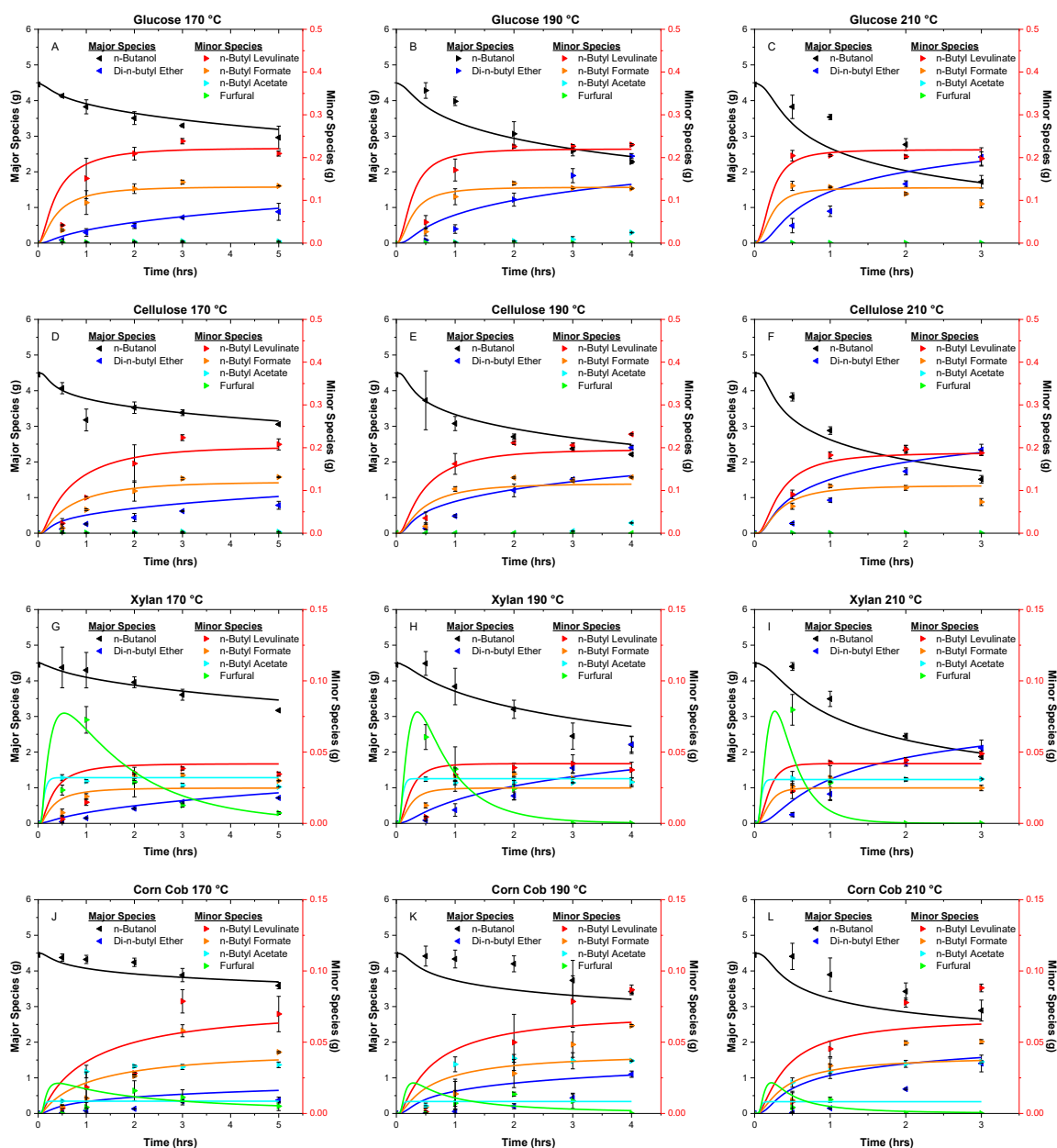


Figure 47. Liquid product concentrations (g) for the acid-catalysed butanolysis of glucose (A-C), cellulose (D-F), xylan (G-I), and corn cob (J-L) at 170, 190, and 210 °C. The triangle symbols represent experimental data points while the lines were produced by the surrogate kinetic model. The uncertainties represent the standard deviation of the four data points collected for each set of experimental conditions.

n-Butyl formate, n-butyl acetate & furfural

Several co-products were consistently or selectively observed during the acid-catalysed butanolysis of biomass-derived substrates, reflecting the complex interplay of primary and secondary reaction pathways under thermochemical conditions.

n-Butyl formate was detected in all reaction mixtures at concentrations slightly lower than *n*-butyl levulinate. Its formation is attributed to the esterification of *n*-butanol with formic acid, a known degradation by-product of C6 sugar pathways associated with levulinate formation (see Reaction 6, Table 19). Its consistent presence underscores the unavoidable coupling of main and side reactions in this system.

In contrast, *n*-butyl acetate was formed in appreciable amounts only in reactions involving xylan and corn cob, where it reached steady-state concentrations up to 41 wt.% relative to *n*-butyl levulinate (Figure 47). Only trace levels were observed in glucose, cellulose, and xylose systems.

This selective formation implies a mechanism involving direct transesterification of acetyl groups from acetylated hemicellulose components with *n*-butanol. ¹H NMR analysis supports this, indicating a degree of acetylation of 0.34 for the xylan used (Section 4.4.3). Comparable yields in corn cob suggest either a higher intrinsic acetylation of embedded xylan or the contribution of acetyl groups from other constituents such as lignin or starch-like polysaccharides.

Furfural, a well-known dehydration product of pentoses, was detected only in xylan and corn cob reactions, consistent with its origin from xylan degradation. It typically appeared at early time points and diminished over time due to further transformation into humins and other non-volatile products. A complementary experiment using furfural as the sole feedstock resulted in rapid polymerisation, precluding gas chromatography analysis, confirming its high reactivity under these conditions.

These observations collectively highlight the influence of feedstock composition on the distribution of both major and minor products. The overlapping formation pathways further emphasise the mechanistic complexity of alcoholysis reactions and the need to consider side reactions when optimising yield and selectivity.

6.5.5 Activation Energy Calculations

Table 16 summarises the activation energies and R² values for two competing reactions in the sulphuric acid-catalysed butanolysis process: (i) the reaction of *n*-butanol with model feedstocks (glucose, cellulose, and xylan) to produce *n*-butyl levulinate, and (ii) the

conversion of *n*-butanol to di-*n*-butyl ether. These data provide valuable insights into reaction selectivity and the reproducibility of the experimental results. It is important to clarify that these calculations are focused on model compounds and do not extend to more complex, real biomass feedstocks.

Table 16. Activation energies (kcal/mol) and corresponding R^2 values from $\ln(1/k)$ vs $1/RT$ plots for the formation of *n*-butyl levulinate from *n*-butanol and various feedstocks, and for the formation of di-*n*-butyl ether from butanol.

Reaction	<i>n</i> -Butanol + Feedstock → <i>n</i> -Butyl Levulinate + Formic acid + Water		<i>n</i> -Butanol + <i>n</i> -Butanol → Di- <i>n</i> -butyl ether + Water	
Feedstock	Activation Energy	R^2	Activation Energy	R^2
Glucose	5.3	0.999	16.7	0.998
Cellulose	8.8	0.981	20.2	0.989
Xylan	10.1	0.989	18.9	0.994

6.5.5.1 *n*-Butyl Levulinate Formation

The activation energies for the *n*-butyl levulinate formation are notably lower across all feedstocks compared to those for di-*n*-butyl ether formation, indicating that *n*-butyl levulinate production is kinetically favoured under appropriate reaction conditions. Glucose exhibited the lowest $E_A = 5.3$ kcal/mol, with an R^2 value of 0.999, reflecting the high consistency of the experimental data. Cellulose and xylan demonstrated higher barriers, 8.8 and 10.1 kcal/mol, respectively, likely due to their polymeric structures, which require higher energies to access their reactive sites. The corresponding R^2 values (0.981 and 0.989) confirm the reliability of the measurements, despite the increased complexity of the feedstock structures.

6.5.5.2 Di-*n*-butyl Ether Formation

In contrast, the activation energies for the formation of di-*n*-butyl ether are significantly higher for all feedstocks, with values of 16.7 kcal/mol for glucose, 20.2 kcal/mol for cellulose, and 18.9 kcal/mol for xylan. These higher barriers suggest that the etherification reaction is less kinetically favourable compared to *n*-butyl levulinate formation, which provides a basis to optimise reaction conditions to selectively enhance the production of the desired alkyl levulinate. The R^2 values for the etherification reaction (0.998, 0.989, and 0.994

for glucose, cellulose, and xylan, respectively) indicate strong consistency in the experimental data, further supporting the robustness of the calculated activation energies. Although these calculations are not frequently performed, some previous works chose this approach to experimentally investigate the thermo-kinetics of diethyl ether production through catalysed alcoholysis. For instance, Tripodi et al. [239] reported an activation barrier of approximately 19 kcal/mol for the dehydration of ethanol to diethyl ether over alumina-based catalysts Aali et al. [240] determined $E_A = 23$ kcal/mol for the same reaction, using a ZSM-5 catalyst. Additionally, Zhu et al. [47] derived an activation barrier of 29 kcal/mol for the formation of diethyl ether during the ethanolysis of glucose catalysed by sulphuric acid.

6.5.5.3 Comparative Analysis and Implications

The lower activation energies for *n*-butyl levulinate formation suggest that, under optimised conditions, such as lower temperatures and minimal acid concentrations, it is possible to selectively catalyse this reaction while suppressing the formation of di-*n*-butyl ether. However, the trends in activation energy also highlight the influence of feedstock structure on reaction kinetics. Glucose, as a simple monosaccharide, requires the least energy for both reactions, while xylan, with its complex hemicellulosic structure, consistently exhibits higher activation energies. This variation highlights the importance of carefully tailoring reaction conditions, such as temperature and catalyst concentration, to the feedstock to achieve optimal selectivity.

The high R^2 values across all datasets demonstrate the consistency of the experimental results, particularly for the di-*n*-butyl ether activation energy calculations. The reliability of these values is attributed to the fact that the di-*n*-butyl ether reaction had not reached equilibrium at any of the measured time points, providing a substantial number of kinetic data points for reliable calculations. In contrast, the activation energy calculations for *n*-butyl levulinate, while also yielding high R^2 values, embody more uncertainty due to the comparatively fewer kinetic phase data points available. This dataset reflects the rapid progression of the *n*-butyl levulinate reaction towards equilibrium, reducing the extent of kinetic information that could be captured.

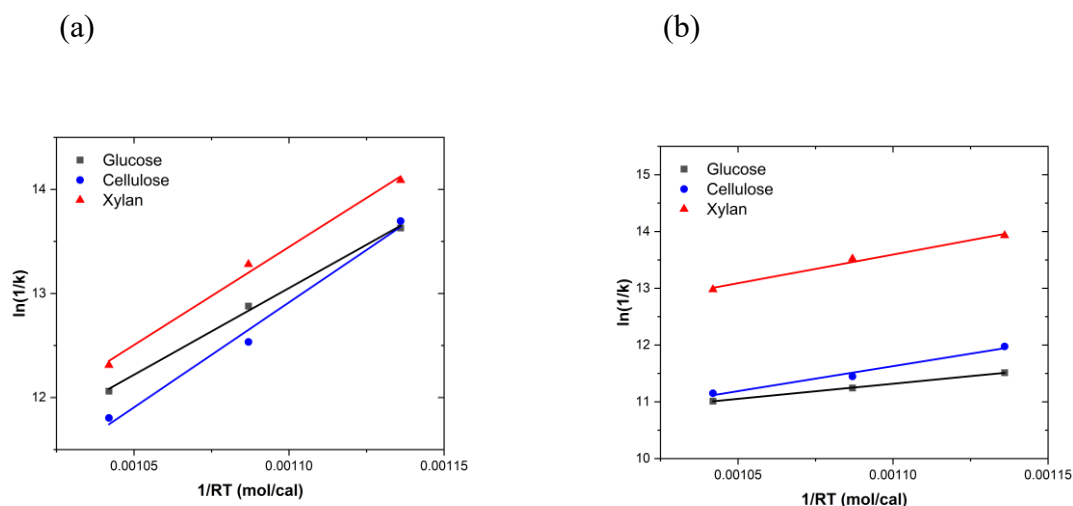


Figure 48. Plots of $\ln(1/k)$ vs $1/RT$ (mol/cal) for the reaction of n-butanol to n-butyl levulinate (panel a) and for n-butanol to di-n-butyl ether (panel b). k is the rate constant, R is the universal constant of the ideal gas, and T is the absolute temperature.

6.5.5.4 Integration of Activation Energies into Surrogate Kinetic Model

The experimentally derived activation energies summarised in Table 16 were incorporated into the surrogate kinetic model to directly connect empirical measurements with modelled reaction pathways. Values obtained from Arrhenius fitting are indicated with an asterisk (*) in Table 19. These assignments ensure that the surrogate model reflects the experimentally observed kinetics while acknowledging the approximations required when mapping global activation barriers onto multi-step mechanisms

For di-n-butyl ether formation, the experimentally determined activation barrier of 16.7 kcal/mol was applied to both the forward etherification step (3f) and the reverse hydrolysis step (3r). This is justified because the Arrhenius analysis tracked the etherification pathway explicitly, and the same barrier governs the reversible process under acid-catalysed conditions

For glucose, the experimentally derived barrier of 5.3 kcal/mol reflects the overall conversion of glucose with butanol to butyl levulinate. In the surrogate model, this transformation is represented by two steps: glucoside formation (Reaction 4, Table 19) and subsequent conversion of the glucoside to butyl levulinate (Reaction 5). The measured barrier was therefore assigned to both steps. This approach provides consistency with the empirical data but should be regarded as a modelling simplification, since the apparent

barrier represents the net kinetics of the overall process rather than discrete mechanistic contributions.

For cellulose, the activation energy of 8.8 kcal/mol was applied to the surrogate steps describing cellulose hydrolysis to glucose (Reaction 9) and the subsequent formation of butyl glucoside (Reaction 10). As with glucose, this represents a pragmatic mapping of a global experimental barrier to multiple surrogate reactions.

For xylan, the experimentally measured barrier of 10.1 kcal/mol was directly assigned to the single surrogate step leading to butyl levulinate (Reaction 15). In this case, the one-step representation aligns closely with the experimental observation, avoiding the ambiguity present in multi-step schemes.

This integration strategy ensures that the surrogate kinetic model is anchored in experimentally validated activation energies, while also maintaining a transparent record of the assumptions involved. The use of asterisks in Table 19 clearly distinguishes values derived from experimental Arrhenius analysis (Table 16) from those that were estimated or fitted, thereby strengthening the traceability of the model.

6.5.6 Humins

6.5.6.1 Humin Composition

The elemental compositions presented in Table 17 illustrate a consistent trend across all feedstocks: the humins formed during butanolysis exhibit elevated carbon content and reduced hydrogen-to-carbon (H/C) molar ratios relative to their biomass source. This shift in composition reflects the increasing aromatic character and condensed structure, typical of humin formation via dehydration and polymerisation reactions under acidic conditions. The substantial decrease in H/C ratio from 1.84 in xylan to 1.12 in xylan-derived humins, for instance, is indicative of greater unsaturation and aromaticity, hallmarks of thermally stable carbonaceous residues.

Table 17. Ultimate analysis (mol%) of feedstocks and corresponding humins formed during butanolysis.

Sample	Carbon	Hydrogen	Nitrogen	Sulphur	H/C
Glucose	3.75	6.44	0.00	0.00	1.72
Glucose humins	5.38	5.55	0.00	0.04	1.03
Cellulose	3.55	6.31	0.00	0.00	1.78
Cellulose humins	4.95	5.78	0.00	0.20	1.17
Xylan	3.47	6.38	0.00	0.00	1.84
Xylan humins	5.19	5.83	0.00	0.08	1.12
Corn cob	3.75	6.44	0.08	0.00	1.72
Corn cob humins	4.03	5.79	0.09	0.13	1.44

Notably, none of the feedstocks contain detectable levels of sulphur, yet the humins contain varying amounts, ranging from 0.04 to 0.20 mol%. This incorporation arises from the use of a sulphuric acid catalyst in the butanolysis process and implies the physical retention of sulphur-containing species during humin formation. While the presence of sulphur may be problematic for some valorisation pathways, its identification here suggests the need for post-processing strategies, such as thermal treatment, washing, or chemical modification, to remove or mitigate sulphur contamination.

Owing to their elemental carbon richness, humins hold promise for a range of applications similar to those of biochar. Potential uses include soil amendment, carbon sequestration, and replacement of peat moss in horticultural substrates [129, 130]. These applications contribute positively to the environmental profile of biorefinery processes by valorising solid residues and reducing the overall life-cycle impact. However, it is essential to note that for soil-related or environmental applications, the sulphur content must be reduced to meet agronomic and regulatory standards, as excessive sulphur can acidify soils or introduce phytotoxicity [132].

Further research should prioritise the molecular characterisation of humins to identify structural features relevant to their reactivity, stability, and functional group availability. This will allow for the development of tailored applications for humins and ensuring they are not treated merely as waste streams, but rather as valuable co-products in lignocellulosic bioconversion pathways.

6.5.6.2 Carbon Molar Yields of Humins

Table 18 presents the molar carbon yields of humins formed during the sulphuric acid-catalysed butanolysis of feedstocks of varying complexity. The carbon yields are calculated assuming that all carbon in the humin fraction originates from the feedstock.

Glucose and cellulose yield relatively modest average carbon contents in humins across the examined temperature range, at 26.5 and 31.9 mol%, respectively. These values are notably lower than the corresponding carbon yields to *n*-butyl levulinate, at 38.9 and 35.9 mol%, indicating that a greater fraction of feedstock carbon is converted into the desired advanced biofuel product than is lost to solid residues under the applied conditions.

Table 18. Carbon Yields (mol%) of humins derived from various feedstocks.

Feedstock	Carbon in humins (wt.%)	170 °C	190 °C	210 °C
Glucose	64.6	24.9	27.7	26.8
Cellulose	59.5	29.6	34.0	32.1
Xylan	61.9	75.1	72.0	67.7
Corn cob	48.4	30.3	33.1	35.1

$$\text{Carbon yield of humins (mol\%)} = \frac{\text{Moles of carbon in humins}}{\text{Moles of carbon in feedstock}} \times 100\% \quad (44)$$

In contrast, corn cob yields humins with an average carbon yield of 32.8 mol%, while only 13.5 mol% of the carbon is recovered as *n*-butyl levulinate. This outcome is expected, as only the polysaccharide fraction (cellulose and hemicellulose), comprising approximately 56.6 wt.% of the biomass, is reactive under alcoholysis conditions. The remainder, primarily lignin and extractives, contributes little to *n*-butyl levulinate formation but may promote side reactions that lead to humin formation. These findings underscore the importance of valorising humins co-produced from lignocellulosic alcoholysis, which show promise for applications as carbon-rich soil conditioners and long-term carbon sequestration materials [131].

Xylan, a hemicellulosic pentosan polymer, yields the highest humin carbon among all feedstocks studied, averaging 71.6 mol%. As shown in Figure 47, xylan rapidly releases furfural at early reaction stages, consistent with literature reports. Furfural is known to

undergo acid-catalysed polymerisation in alcoholic solvents [241], contributing substantially to the mass of the resulting insoluble humin fraction. This behaviour may explain the disproportionate humin yield observed for xylan relative to other substrates.

6.5.7 Composition of Product Mixture

The product mixtures from the sulphuric acid-catalysed butanolysis of glucose, cellulose, xylan, and corn cob (10 wt.%) at varying temperatures (170, 190, and 210 °C) and reaction times highlight the importance of optimising reaction conditions to maximise the desired *n*-butyl levulinate while minimising the formation of di-*n*-butyl ether and other by-products. Across all feedstocks, *n*-butyl levulinate mass fractions were highest for glucose and cellulose, with maximum values of 4.5 wt.% of the product mixture each at lower reaction temperatures (170–190 °C). Xylan and corn cob, in contrast, showed significantly lower *n*-butyl levulinate mass fractions of 0.9 and 1.6 wt.% of the product mixture, when using a feedstock loading of 10 wt.%. This is attributed to their lower glucan content and more complex structures. Figure 49 shows the full product mixtures (wt.%) as well as a focused view excluding *n*-butanol for improved resolution of minor species. Although higher masses of *n*-butyl levulinate in the product mixture are desirable, achieving them can be challenging. Preliminary experiments using feedstock loadings of 20 wt.% resulted in highly viscous product mixtures, with higher humin concentrations and insufficient supernatant to allow for accurate and reliable determination of product concentrations. Therefore, moderate feedstock loadings are recommended for butanolysis reactions involving lignocellulosic biomass

Identification of minor species

In addition to the primary products, *n*-butyl levulinate, *n*-butanol, and di-*n*-butyl ether, *n*-butyl formate was identified in the product mixtures from all four feedstocks examined in this study. *n*-Butyl formate, which forms via the esterification of formic acid and butanol, was detected in notable concentrations, reaching up to 74 wt.% relative to *n*-butyl levulinate. Formic acid is a well-established by-product of ethyl levulinate formation, as reported in previous studies [44, 87, 124], and is likewise expected to form under analogous butanolysis

conditions. Its presence in the system therefore provides a clear mechanistic route for the formation of *n*-butyl formate, as illustrated in Reaction 6 in Table 19.

n-Butyl acetate and furfural were also identified in the product mixtures from xylan and corn cob. Their formation is attributed to the acetyl groups present in these feedstocks, as discussed in Section 4.4.3, and to the depolymerisation and subsequent dehydration of xylan monomers, which generate furfural at short reaction times. All species identified were confirmed through mass spectrometry. Their formation pathways are incorporated into the surrogate kinetic model through a simplified reaction scheme designed to account for minor side reactions.

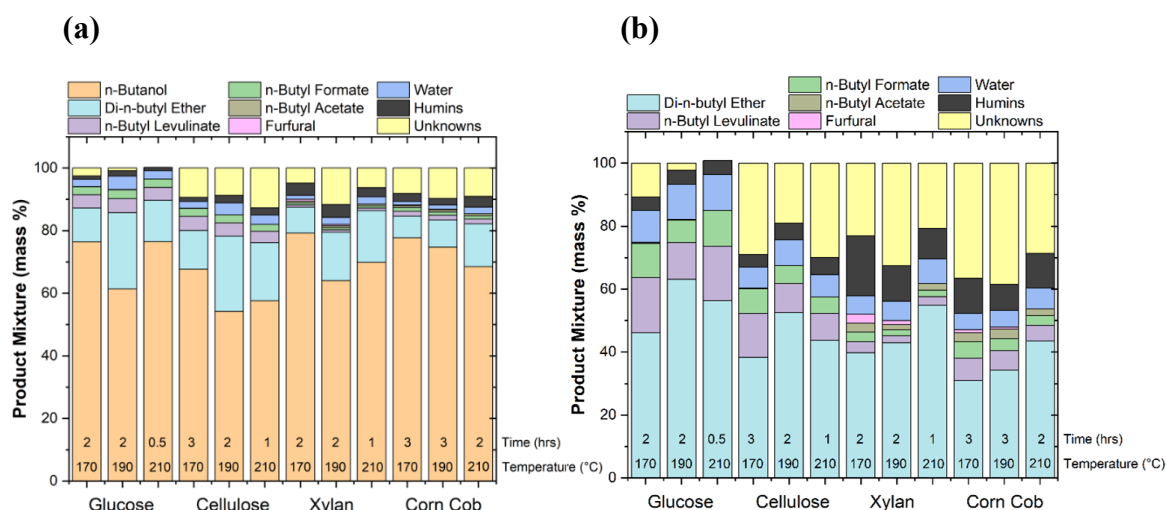


Figure 49. Product mixtures (wt.%) for the acid-catalysed butanolysis of glucose, cellulose, xylan, and corn cob at 170, 190, and 210 °C. The time-points correspond to the shortest intervals at which steady-state was achieved for *n*-butyl levulinate formation. In panel a: the full product mixture. In panel b: the product mixture excludes *n*-butanol for better resolution of minor species.

Reaction mixture composition

A critical observation is the trade-off in formation between *n*-butyl levulinate and di-*n*-butyl ether. Higher temperatures and longer reaction times favour di-*n*-butyl ether production, particularly for glucose and cellulose, with mass fractions reaching 24.4 and 24.1 wt.% at 190 °C, respectively, even at the earliest steady-state conditions of levulinate production. It is important to note that the reported mass fractions reflect the composition of these products in the reaction mixture rather than their actual yields. This underscores the need to optimise reaction conditions to maximise *n*-butyl levulinate formation while limiting

di-*n*-butyl ether production, which not only consumes valuable alcohol but also reduces atom economy and process sustainability. Notably, di-*n*-butyl ether generation contributes to the water content of the reaction mixture, with mass fractions reaching up to 4.3 wt.% (glucose at 190 °C). The presence of water complicates downstream separation and can shift equilibria unfavourably, promoting reverse hydrolysis of esters and lowering overall levulinate yields. Therefore, minimising water formation, through careful control of reaction pathways or integrating water removal strategies, represents a critical target for improving the efficiency and green metrics of the butanolysis process.

Value of by-products

While di-*n*-butyl ether is generally considered an undesired by-product in this context, it holds potential as an additive for diesel fuel. When used at controlled concentrations, it improves cold flow properties and enables the formulation of blends that meet fuel property standards such as flash point, density, and viscosity [41]. Therefore, at moderate concentrations it can enhance the overall atom efficiency of the butanolysis process, positioning it as a valuable co-product.

Conversely, *n*-butyl acetate is utilised across multiple sectors. It serves as a solvent in the production of adhesives, lacquers, coatings, and paints, contributing to the manufacture of consumer products such as automobiles and wood furniture. In the pharmaceutical and cosmetic industries, it functions as an extraction agent or solvent, while in the food industry, it is employed to synthesize fruit flavours. Additionally, *n*-butyl acetate has been explored as a biofuel additive, with studies indicating that its inclusion in biodiesel blends can reduce soot and greenhouse gas emissions without adversely affecting combustion heat and cetane number [242, 243].

Moreover, *n*-butyl formate has been investigated for its potential as a biofuel, with studies examining its combustion behaviour, such as ignition delay and laminar flame speed, highlighting its suitability as an alternative fuel component [244]. Additionally, its occurrence in fruits like apples and strawberries highlights its potential application in the flavour and fragrance industries [245]. These diverse uses underscore the economic value of *n*-butyl formate as a by-product of the process.

Furfural, derived from lignocellulosic biomass, serves as a versatile platform chemical with numerous industrial applications. It is widely used to produce resins and adhesives, particularly within the plastics and coatings industries [237]. In the pharmaceutical sector, furfural acts as a precursor for various medicinal compounds, while in agriculture, it contributes to the synthesis of herbicides and nematicides [238]. Additionally, furfural functions as a selective solvent in refining processes, particularly for lubricating oils and the extraction of dienes in synthetic rubber manufacture. However, under the acidic, moderate-temperature conditions typical of butanolysis, furfural may also undergo polymerisation, contributing to the formation of humins. These insoluble carbonaceous by-products which may contain these furanic structures. Thus, while furfural valorisation presents a promising route to enhance process economics, its role in humin formation must also be considered in the context of product yield and carbon efficiency but is beyond the scope of this paper.

This analysis highlights the potential for refining the reaction system to selectively enhance the mass fraction of *n*-butyl levulinate while simultaneously leveraging by-product valorisation strategies. These efforts, combined with the predictive power of the surrogate kinetic model, can improve the sustainability and profitability of advanced biofuel production. By designing reaction systems that maximise desired products while valorising side products, the prevention of waste is targeted in alignment with Green Chemistry principles. Given its impact on both thermodynamic equilibrium and process economics, water generation should also be considered a key optimisation target, alongside humin suppression and alcohol preservation, in future butanolysis system design. Identifying valuable co-products such as *n*-butyl acetate, di-*n*-butyl ether, and furfural exemplifies how comprehensive systems analysis can reveal opportunities for integrated biorefinery designs, further enhancing environmental and economic sustainability.

6.5.8 Hierarchical Biochemical Surrogate Kinetic Model

6.5.8.1 Developments from Previous Models

The butanolysis surrogate kinetic model presented here builds upon earlier ethanolysis versions [44, 124], incorporating several key advancements to improve predictive capability and mechanistic accuracy.

First, the model has been newly trained using acid solvolysis data obtained in *n*-butanol solvent systems, enabling its application to both ethanolysis and butanolysis reactions.

Second, the model has been extended to predict the yields of all non-trace products in the reaction mixture, including *n*-butyl levulinate, di-*n*-butyl ether, butanol, furfural, butyl acetate, formic acid, butyl formate, humins, and water.

Third, the model ensures strict mass conservation with the unaccounted mass categorised as “soluble unknowns”, representing a diverse array of trace species solubilised in the reaction medium. Distinct compositions of soluble unknowns are associated with each feedstock; glucose, cellulose, xylan monomer, acetylated xylan monomer, furfural, and residual corn cob biomass (comprising lignin, ash, extractives, and other unidentified constituents) (Figure 50). While the precise molecular identities of these soluble unknowns are unresolved, their grouped elemental composition provides insight into the likely classes of trace species present. For every humin-forming pathway, a corresponding route to a unique soluble unknown composition is included, thereby ensuring overall mass conservation.

Fourth, each pathway leading to the formation of humins, or soluble unknowns, is represented by two parallel reactions: one catalytic (regenerating hydrogen ions) and one non-catalytic (consuming hydrogen ions). This structure captures the acid consumption phenomenon observed in the acid-catalysed alcoholysis of lignocellulosic biomass [44].

Finally, the kinetic parameters including pre-exponential factors, activation energies, and rate constants are summarised in Table 19. These were optimised using the algorithm described in Section 3.7.4. However, the activation energies for reactions 3f, 3r, 4, 5, 9, 10, and 15 were calculated directly as detailed in Section 6.5.5 and input into the model before parameter optimisation for the remaining reactions.

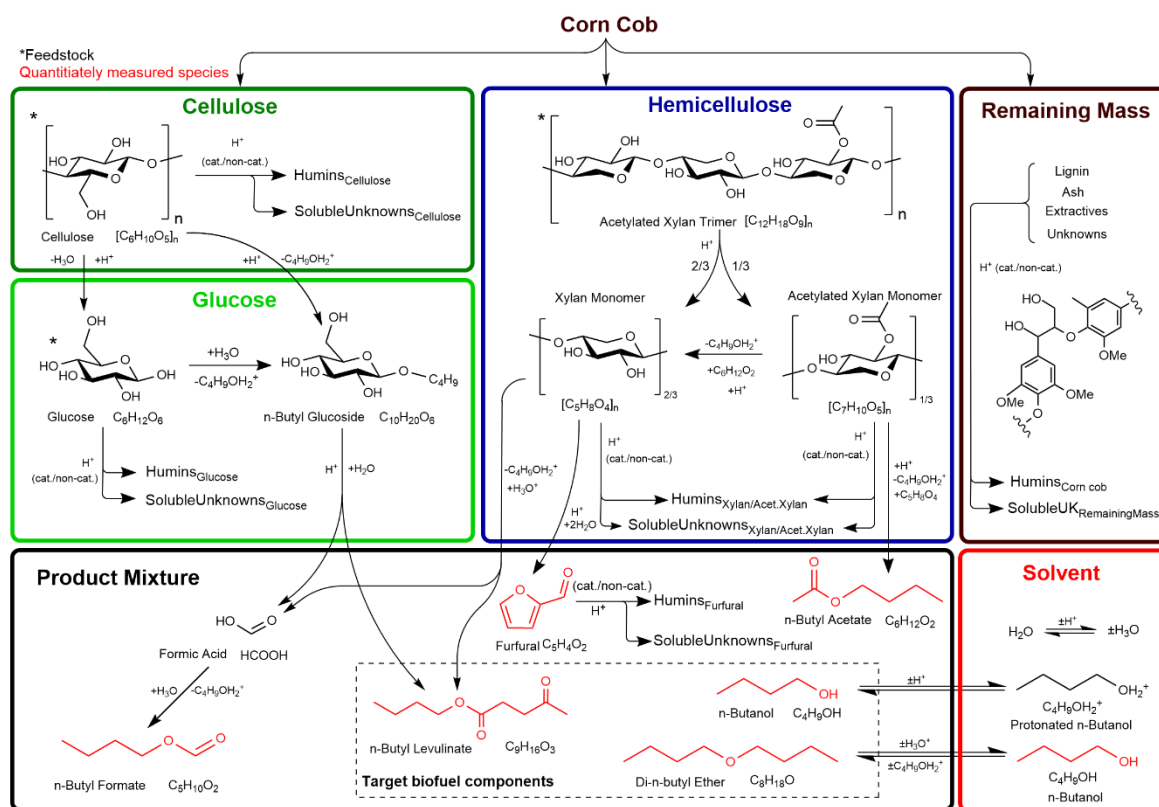


Figure 50. Hierarchical surrogate kinetic model for butanolysis, illustrating the proposed reaction mechanism and hierarchical sub-models. Associated reaction equations are provided in Table 19. Humins are dark-coloured, insoluble by-products formed during alcoholysis, while unknowns, determined by mass balance, represent other soluble species of unidentified structural composition. The representative lignin structure is adapted from Wang et al. [246].

6.5.8.2 Novel Product Predictions: Furfural, *n*-Butyl Acetate, and *n*-Butyl Formate

The surrogate kinetic model successfully predicts the concentrations of all six major value-added products formed in the butanolysis reaction mixture. In particular, the early formation of furfural and its subsequent decomposition to insoluble solid residues (humins) is well replicated. The formation profile of *n*-butyl formate is also accurately captured by the model.

Among the three novel products, *n*-butyl acetate presents the greatest modelling challenge, particularly when applying the surrogate model to the complex corn cob feedstock. In the model, *n*-butyl acetate formation is described by an esterification reaction between an acetylated xylan monomer and a molecule of *n*-butanol, yielding one molecule of *n*-butyl acetate and a deacetylated xylan monomer. The degree of xylan acetylation, 33%,

Chapter 6. Butanolysis

was quantified by NMR spectroscopy and is reported in Section 4.4.3. Therefore, the xylan is modelled with one acetyl group per trimer.

Table 19. List of reactions included in the butanolysis surrogate kinetic model with their corresponding derived empirical kinetic parameters

#	Reaction	A ($\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$)	E _A (kcal/mol)	K @190 °C ($\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$)
1f	Butanol + H ⁺ → Butanol/H ⁺	2.0 x 10 ⁷	6.0	2.94 x 10 ⁻⁴
1r	Butanol/H ⁺ → Butanol + H ⁺	2.0 x 10 ⁴	6.0	2.94 x 10 ⁻¹
2f	H ₂ O + H ⁺ → H ₃ O ⁺	1.0 x 10 ⁶	2.0	1.14 x 10 ⁻⁵
2r	H ₃ O ⁺ → H ₂ O + H ⁺	1.0 x 10 ⁶	15.5	4.82 x 10 ⁻²
3f	Butanol + Butanol/H ⁺ → Di-n-butyl ether + H ₃ O ⁺	1.5 x 10 ⁶	16.7*	1.96 x 10 ⁻²
3r	Di-n-butyl ether + H ₃ O ⁺ → Butanol + Butanol/H ⁺	3.0 x 10 ¹	16.7*	3.92 x 10 ⁻⁷
4	Glucose + Butanol/H ⁺ → Butyl glucoside + H ₃ O ⁺	9.0 x 10 ¹	5.3*	2.83 x 10 ⁻¹
5	Butyl glucoside + Butanol/H ⁺ → Butyl levulinate + Formic acid + H ₂ O + Butanol/H ⁺	1.4 x 10 ²	5.3*	4.41 x 10 ⁻¹
6	Formic acid + Butanol/H ⁺ → Butyl formate + H ₃ O ⁺	1.5 x 10 ⁵	4.9	7.29 x 10 ⁻²
7	Glucose + H ⁺ → Humins_Glucose + SolubleUnknowns_Glucose + H ⁺	5.8 x 10 ⁰	5.6	1.32 x 10 ⁻²
8	Glucose + H ⁺ → Humins_Glucose + SolubleUnknowns_Glucose/H ⁺	2.0 x 10 ⁻⁵	4.8	1.08 x 10 ⁻⁷
9	Cellulose + H ₃ O ⁺ → Glucose + H ⁺	5.6 x 10 ¹	8.8*	3.93 x 10 ⁻³
10	Cellulose + Butanol/H ⁺ → Butyl glucoside + H ⁺	7.6 x 10 ²	8.8*	5.33 x 10 ⁻²
11	Cellulose + H ⁺ → Humins_Cellulose + SolubleUnknowns_Cellulose + H ⁺	7.0 x 10 ¹	9.2	3.18 x 10 ⁻³
12	Cellulose + H ⁺ → Humins_Cellulose + SolubleUnknowns_Cellulose/H ⁺	5.6 x 10 ¹	9.8	1.32 x 10 ⁻³
13	Acetylated Xylan Trimer + H ⁺ → 2 Xylan Monomer + Acetylated Xylan Monomer + H ⁺	5 x 10 ⁷	17.0	4.72 x 10 ⁻¹
14	Acetylated Xylan Monomer + Butanol/H ⁺ → Xylan Monomer + n-Butyl acetate + H ⁺	1.6 x 10 ⁴	9.0	9.03 x 10 ⁻¹
15	1.2 Xylan Monomer + Butanol/H ⁺ → Butyl levulinate + Formic acid + 0.8 H ₂ O + H ⁺	5.6 x 10 ⁴	10.1*	9.56 x 10 ⁻¹
16	Xylan Monomer + H ⁺ → Furfural + 2 H ₂ O + H ⁺	6.5 x 10 ²	9.7	1.71 x 10 ⁻²
17	Xylan Monomer + H ⁺ → Humins_XylanMonomer + SolubleUnknowns_XylanMonomer + H ⁺	9.8 x 10 ⁰	10.1	1.67 x 10 ⁻⁴
18	Xylan Monomer + H ⁺ → Humins_XylanMonomer + SolubleUnknowns_XylanMonomer/H ⁺	3.8 x 10 ¹	9.5	1.24 x 10 ⁻³
19	Acetylated Xylan Monomer + H ⁺ → Humins_AcetylatedXylanMonomer + SolubleUnknowns_AcetylatedXylanMonomer + H ⁺	2.3 x 10 ⁴	11.0	1.48 x 10 ⁻¹
20	Acetylated Xylan Monomer + H ⁺ → Humins_AcetylatedXylanMonomer + SolubleUnknowns_AcetylatedXylanMonomer/H ⁺	8.8 x 10 ²	10.6	8.72 x 10 ⁻³
21	Furfural + H ⁺ → Humins_Furfural + SolubleUnknowns_Furfural + H ⁺	2.8 x 10 ²	8.9	1.76 x 10 ⁻²
22	Furfural + H ⁺ → Humins_Furfural + SolubleUnknowns_Furfural/H ⁺	1.1 x 10 ⁻⁶	9.5	3.60 x 10 ⁻¹¹
23	Corn cob + H ⁺ → 0.336 Acetylated Xylan Trimer + Cellulose + Remaining Mass + H ⁺	1.0 x 10 ⁵	0.0	1.00 x 10 ⁻⁵
24	Remaining Mass + H ⁺ → Humins_RemainingMass + SolubleUnknowns_RemainingMass + H ⁺	8.6 x 10 ⁻⁴	5.6	1.95 x 10 ⁻⁶
25	Remaining Mass + H ⁺ → Humins_RemainingMass + SolubleUnknowns_RemainingMass/H ⁺	4.2 x 10 ⁻¹	4.2	4.37 x 10 ⁻³

In the butanol sub-model, f and r denote forward and reverse reactions. Activation energy values marked with an asterisk (*) were experimentally determined from Arrhenius fitting (see Table 16) and mapped to the surrogate reactions as described in Section 6.5.5. Species and pathways are defined in Figure 50.

When xylan was used as the feedstock, the predicted *n*-butyl acetate concentrations closely matched the experimental data. However, corn cob produced comparable concentrations of *n*-butyl acetate despite xylan comprising only approximately 24.2 wt.% of the corn cob biomass. This outcome was unexpected, as the *n*-butyl acetate yield would be anticipated to scale with the xylan content. These results suggest that either unprocessed corn

cob contains xylan with a higher degree of acetylation or that additional acetyl-containing components in the corn cob, most likely lignin, contribute to *n*-butyl acetate formation under the reaction conditions. Consequently, the model underpredicts *n*-butyl acetate yields for corn cob feedstock, as it currently attributes esterification exclusively to xylan-derived acetyl groups.

6.5.8.3 Hierarchical Biochemical Surrogate Kinetic Model

Figure 47 presents the concentration–time profiles of the principal liquid products obtained from butanolysis, alongside predictions from the surrogate kinetic model. The model demonstrates strong agreement with the experimental data across most species, accurately replicating the behaviour of *n*-butanol ($R^2 = 0.99$), di-*n*-butyl ether ($R^2 = 0.91$), *n*-butyl levulinate ($R^2 = 0.92$), and *n*-butyl formate ($R^2 = 0.94$). Similarly, the concentration of *n*-butyl acetate is predicted with high fidelity for model substrates ($R^2 = 0.95$), although notable deviations arise in the case of corn cob. As previously discussed, this discrepancy reflects the release of acetyl groups from both hemicellulose and lignin, which are not fully incorporated into the current model configuration.

Table 20. Coefficients of determination (R^2) for the major products of the butanolysis system.

	<i>n</i> -Butanol	Di- <i>n</i> -butyl Ether	<i>n</i> -Butyl Levulinate	<i>n</i> -Butyl Formate	<i>n</i> -Butyl Acetate	Furfural
R^2	0.99	0.91	0.92	0.94	0.95	0.62

The weakest correlation was observed for furfural ($R^2 = 0.62$), highlighting the challenge of fully capturing hemicellulose degradation and subsequent side-reactions leading to humin formation. These outcomes are further illustrated in Figure 49 (Section 6.5.7), which depicts the complete composition of the liquid product mixtures under steady-state conditions.

Taken together, these results demonstrate that the butanolysis hierarchical surrogate kinetic model provides a reliable and practical framework for evaluating biomass butanolysis systems. By enabling quantitative prediction of value-added liquid products based solely on the biochemical composition of the feedstock, the model offers significant utility for both life-cycle assessment and techno-economic assessment. Such predictive capability facilitates rational process optimisation and feedstock prioritisation, thereby accelerating the commercial readiness of alcoholysis technologies.

Crucially, the model supports the strategic assessment of diverse lignocellulosic resources, enabling efficient allocation of biomass streams to maximise product yields and carbon efficiencies. The resulting three-component fuel mixtures have demonstrated compatibility with both diesel and gasoline engines, with stable blending at concentrations up to 25% [41]. These findings underline the potential of alcoholysis-derived fuel blends to reduce greenhouse gas emissions across passenger and heavy-duty transport sectors. Championing scale-up and deployment of this pathway, underpinned by robust mechanistic modelling, is therefore vital to advancing transport decarbonisation objectives.

6.5.8.4 Predicted Space-Time Yields at T_{90}

The hierarchical biochemical surrogate kinetic model was used to estimate yields of *n*-butyl levulinate and di-*n*-butyl ether across various feedstocks and temperatures. As a performance metric, space-time yield quantifies the mass of product formed per unit reactor volume per unit time. It is commonly used to assess process productivity and scalability in chemical engineering [235, 247, 248]. In this study, space-time yield was calculated at the time required to reach 90% of the maximum predicted *n*-butyl levulinate yield (T_{90}), which was defined as a practical steady-state condition.

Higher temperatures consistently reduced T_{90} , due to faster reaction kinetics. However, this acceleration came with a trade-off: increased di-*n*-butyl ether formation at higher temperatures, even at the reduced T_{90} reaction times. For example, in the glucose system, raising the temperature from 170 °C to 210 °C decreased T_{90} from 1.4 h to 0.6 h and increased space-time yield from 8.4 to 19.2 g L⁻¹ h⁻¹, while the di-*n*-butyl ether yield more than doubled (from 0.45 to 0.98 g), a side reaction that not only consumes the costly alcohol but also generates water, which must be removed. This selectivity–intensification trade-off was observed across all feedstocks studied, with varying magnitudes. Notably, the quantity of humins isolated at T_{90} remained consistent across temperatures, indicating that shorter reaction durations at higher temperatures do not significantly affect the extent of humin formation.

Table 21. Hierarchical biochemical surrogate kinetic model predictions.

Feedstock	Reactor size (mL)	Temp. (°C)	Max. BL yield (g)	0.9*BL (g)	T90 (hrs)	<i>n</i> -DBE yield at T90 (g)	Humin yield at T90 (g)	Space-time yield (g ^L h ⁻¹)
Glucose	17.5	170	0.221	0.199	1.4	0.45	0.08	8.4
		190	0.220	0.198	0.9	0.70	0.08	13.3
		210	0.218	0.196	0.6	0.98	0.08	19.2
Cellulose	17.5	170	0.199	0.179	2.1	0.71	0.10	4.9
		190	0.193	0.174	1.5	1.06	0.10	6.9
		210	0.186	0.168	1.0	1.52	0.11	9.4
Xylan	17.5	170	0.042	0.038	1.1	0.32	0.17	2.0
		190	0.042	0.038	0.6	0.39	0.17	3.7
		210	0.042	0.038	0.4	0.44	0.17	5.6
Corn cob	17.5	170	0.063	0.057	3.1	0.54	0.09	1.1
		190	0.064	0.058	2.2	0.87	0.10	1.5
		210	0.063	0.056	1.7	1.31	0.10	2.0

Predicted optimal yields, time to reach 90% of maximum yield (T_{90}), di-*n*-butyl ether (*n*-DBE) formation, and space-time yields for *n*-butyl levulinate production from various feedstocks. Simulations assume 10 wt.% feedstock, 1 wt.% sulphuric acid catalyst, and 89 wt.% *n*-butanol. Reactions were conducted in a 17.5 mL liner, approximately one-third filled. Results reflect the modelled reaction conditions and are not optimised for reactor performance.

These findings highlight the need to carefully balance conversion rate and selectivity when optimising reaction conditions. A detailed techno-economic analysis will be required to evaluate whether the gains in space-time yield at higher temperatures are sufficient to offset the increased formation of side products and their associated separation and environmental costs.

6.6 Conclusions

We have systematically evaluated the sulphuric acid-catalysed butanolysis as a viable thermochemical pathway to produce *n*-butyl levulinate, a promising advanced biofuel and platform chemical, utilising diverse biomass-derived feedstocks. By investigating glucose (a monosaccharide), cellulose and xylan (key polysaccharide components), and corn cob (real-world lignocellulosic biomass), at 10 wt% feedstock, 1 wt% H₂SO₄ and 170–210 °C the influence of feedstock composition on reaction efficiency, conditions, and product distribution was determined.

n-Butyl levulinate yields were found to vary depending on the feedstock type, with maximum yields of (49.6 ± 2.7) mol% for glucose at 170 °C, (43.4 ± 0.7) mol% for cellulose at 190 °C, (28.8 ± 3.1) mol% for corn cob at 210 °C, and (8.9 ± 3.7) mol% for xylan at 210 °C. These differences highlight the variability in conversion efficiency, underscoring the need to tailor reaction conditions to the structural and compositional characteristics of each substrate. While elevated temperatures facilitated depolymerisation and sugar release, they also fostered side reactions, underscoring the trade-off between maximising *n*-butyl levulinate yields and minimising by-products. Steady-state times tended to increase with both feedstock complexity and decreasing reaction temperatures, reflecting the kinetic barriers posed by the lignocellulose matrix. Shorter reaction times minimised di-*n*-butyl ether formation, illustrating the importance of identifying the earliest steady-state point for optimal techno-economic outcomes.

Because *n*-butyl levulinate originates from both cellulose and hemicellulose fractions, reporting yields based solely on cellulose content can significantly overestimate process efficiency. This study therefore adopts a more representative method: molar yields are calculated relative to the theoretical maximum based on the total cellulose and hemicellulose content. This approach enables more accurate benchmarking of lignocellulosic feedstock performance and is proposed as a standard for future reporting of molecular product yields from complex biomass sources.

Minor by-products, including *n*-butyl formate, *n*-butyl acetate, and furfural, were consistently detected in the butanolysis of xylan and corn cob. While these compounds typically appear in lower quantities, their concentrations can become significant under steady-state conditions for the production of *n*-butyl levulinate. For instance, *n*-butyl formate reached 74 wt.% and *n*-butyl acetate 41 wt.% relative to levulinate formation in the case of corn cob at the earliest steady-state conditions. These by-products, often overlooked in the literature, may have substantial implications for the economic viability of the process, highlighting the need for careful quantification and potential valorisation as solvents, chemical intermediates, or fuel additives. The detection of *n*-butyl acetate in product mixtures derived from both xylan and corn cob indicated the presence of acetyl groups within the hemicellulose fraction of the biomass. This observation was corroborated by quantitative ^1H NMR, which quantified a mean monomer-based degree of acetylation of 0.34.

The hierarchical biochemical surrogate kinetic model developed herein builds upon prior iterations by incorporating novel features such as mass-conserving product pathways, catalytic and non-catalytic humin formation mechanisms, and grouped soluble unknown species to account for trace mass. The model successfully predicted the yields of all major and minor products, including furfural, *n*-butyl formate, and *n*-butyl acetate. Notably, the model highlighted a key discrepancy in *n*-butyl acetate prediction from corn cob feedstock, suggesting that acetylated moieties within the non-carbohydrate constituents of the biomass, such as lignin, may also contribute to ester formation, an area warranting further investigation. By enabling accurate product yield prediction from biomass composition alone, the model provided a valuable tool for life-cycle assessment, techno-economic analysis, and process optimisation. It facilitated strategic feedstock screening to maximise carbon efficiency and supports the design of scalable systems capable of producing three-component biofuel mixtures (alkyl levulinate, dialkyl ether, and alcohol) shown to be compatible with diesel and gasoline engines at up to 25 vol% blends [41]. These findings have direct relevance to the decarbonisation of both light-duty and heavy-duty transport sectors.

This study demonstrated that one-pot butanolysis of lignocellulosic biomass can be tuned to selectively produce *n*-butyl levulinate and other high-value co-products, with viable yields and robust kinetic modelling support. Industrial scalability will depend on continued efforts in catalyst recovery, continuous-flow processing, and valorisation of all carbon-containing fractions, including humins. Our butanolysis surrogate kinetic model can provide a strong foundation for future simulation-driven optimisation, ultimately enabling more efficient and economically attractive routes to renewable fuel production in an integrated biorefinery context.

Chapter 7

Conclusions and Outlook

7.1 Overall Conclusions

This thesis has demonstrated that acid-catalysed alcoholysis of lignocellulosic biomass is a technically robust and strategically relevant route for advanced biofuel production. By combining feedstock characterisation, experimental investigation, and kinetic modelling, it shows that alcoholysis can transform Annex IX residues into fuel blends compatible with existing infrastructure, directly addressing the challenge of decarbonising hard-to-electrify transport sectors.

The alcoholysis studies revealed that both cellulose and hemicellulose fractions contribute significantly to levulinate yields, challenging the conventional cellulose-centric perspective and enabling a more accurate evaluation of agricultural residues. This recognition expands the pool of sustainable raw materials and strengthens the policy case for hemicellulose valorisation under EU legislation. In addition to this, a further novel finding was the quantification of acid consumption by real lignocellulosic biomass, highlighting a previously underappreciated factor that strongly influences process efficiency, catalyst requirements, and ultimately techno-economic feasibility.

A central methodological contribution is the introduction of steady-state yield analysis. Unlike transient maxima, steady-state values capture the thermodynamically preferred balance of products, providing a rigorous and reproducible standard for process evaluation. The ethanolysis study also revealed that solvent effects, particularly ether formation, exert a strong influence on carbon efficiency, an often-overlooked factor with major techno-economic implications.

Complementing these advances, a surrogate kinetic model was developed based on hierarchical learning and group additivity principles. This reconciles experimental data with predictive simulations and provides a transferable framework that can be applied across diverse substrates and solvents, linking laboratory findings with predictive process modelling.

Motivated by findings from the literature and the SusLABB project context, the butanolysis study extended this foundation by developing a new yield representation framework that incorporates both cellulose and hemicellulose contributions, providing a benchmark for transparent reporting of biomass conversion efficiencies. It also delivered the first systematic identification of secondary co-products, including formates, acetates, and furfural, extending the known product spectrum of alcoholysis. Recognising and quantifying these additional streams improves the accuracy of carbon balances for process modelling and reveals new opportunities for co-product valorisation that can strengthen the commercial competitiveness of alcoholysis-based biorefineries.

Taken together, the ethanolysis and butanolysis studies define a coherent framework. Ethanolysis provided mechanistic clarity, steady-state analysis, and modelling methodology, while butanolysis broadened the product spectrum and developed mechanistic complexity and detail. Both studies quantified the ternary product mixtures of levulinate, ether and alcohol. These mixtures can be used directly as blending components, avoiding costly separations and underlining the immediate applicability of alcoholysis within existing petrol and diesel infrastructures.

At the broadest level, the thesis contributes both to science and to society. Scientifically, it establishes steady-state yield analysis and improved yield representation as methodological standards, develops mechanistically faithful kinetic models, quantifies acid consumption by lignocellulosic biomass, and generates unprecedented data on co-product distributions. Societally, it demonstrates that waste lignocellulosic biomass can be transformed into sustainable fuel blends that support EU RED II/RED III and Ireland's Climate Action Plan. By valorising agricultural residues, alcoholysis offers a pathway to scalable, low-cost, and infrastructure-compatible fuels, strengthening its role as a credible option for near-term decarbonisation and a building block for future bioeconomies. These

advances, taken together, establish the scientific and methodological foundations that underpin the contributions to the field described in the next section.

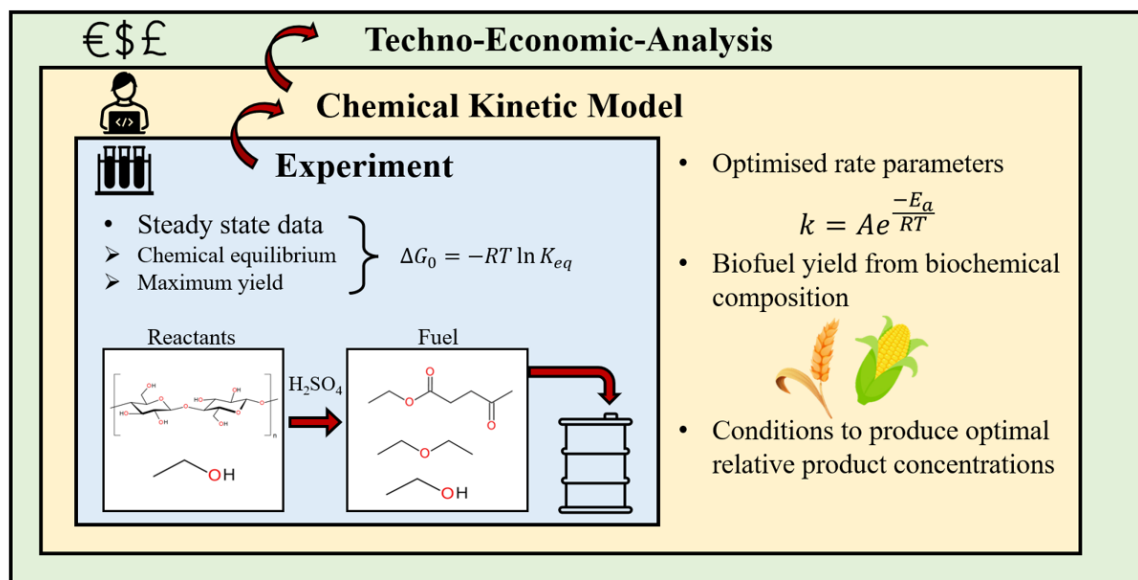


Figure 51. Conceptual overview of this thesis linking experimental alcoholysis studies, steady-state kinetic modelling, and techno-economic analysis. “Experiments established maximum (operational) steady-state yields under the studied conditions, while the surrogate kinetic model predicted biofuel yields from biochemical composition and optimised rate parameters. Together, these advances enable identification of process conditions that maximise relative product concentrations and provide realistic inputs for techno-economic and life-cycle assessments.

7.2 Contribution to the Field

This thesis makes three fundamental contributions that reshape how alcoholysis is evaluated and applied.

First, it establishes steady-state yield analysis as a new standard for assessing alcoholysis reactions. By identifying the equilibrium point at which product concentrations plateau, this approach confirms maximum achievable yields. In contrast, most previous studies reported values at arbitrary time points, without distinguishing between transient kinetics and true process limits. This thesis therefore resolves a long-standing source of inconsistency in the literature, ensuring that alcoholysis performance can be compared on a rigorous and reproducible basis.

Second, the research provides the first demonstration that alkyl levulinates originate from both cellulose and hemicellulose fractions of lignocellulosic biomass. Conventional frameworks attributed levulinate formation solely to cellulose, systematically undervaluing the potential of hemicellulose-rich residues. By introducing a new yield representation that

accounts for the full carbohydrate fraction, this work delivers a more accurate measure of biomass-to-fuel efficiency and expands the range of residues that can credibly be valorised under Annex IX sustainability criteria.

Third, the thesis develops surrogate kinetic models enhanced by hierarchical learning and molecular group additivity principles. This framework balances mechanistic fidelity with predictive power, enabling the chemistry of alcoholysis to be generalised across substrates of increasing complexity. Because it is grounded in transferable structural descriptors, the approach can be extended to other feedstocks and even to other biomass conversion technologies. In doing so, it creates the basis for coupling reaction modelling with techno-economic and life-cycle assessments, allowing product distributions to be optimised for both efficiency and sustainability outcomes.

Taken together, these contributions provide the field with new methodological standards, a broader recognition of biomass reactivity, and a transferable modelling paradigm. They move alcoholysis research beyond isolated case studies toward a systematic, predictive, and industrially relevant discipline, one capable of guiding both scientific discovery and the commercial deployment of advanced biofuels.

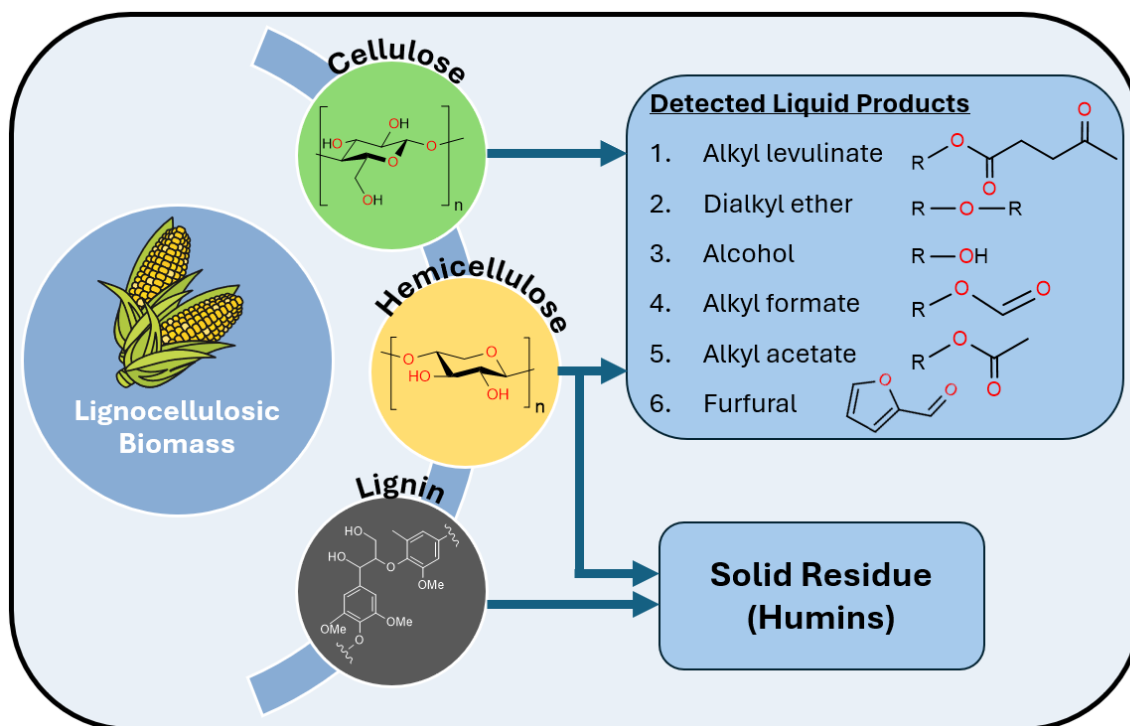


Figure 52. Overview of detected products formed during the alcoholysis of lignocellulosic biomass, including major liquid fractions (alkyl levulinate, dialkyl ether, alcohol, alkyl formate, alkyl acetate, and furfural) and solid residues (humins). The surrogate kinetic model developed in this work is capable of replicating the concentration profiles of all these products.

7.3 Outlook and Future Work

The findings of this thesis open several promising directions for further investigation. These opportunities lie in catalyst development, feedstock diversity, process scale-up, and techno-economic integration, each of which will be essential to move alcoholysis from laboratory study to industrial application.

7.3.1 Catalyst Development and Recyclability

A decisive step in advancing alcoholysis towards commercialisation is the replacement of strong homogeneous acids such as H_2SO_4 with solid, recyclable acid catalysts. Y-type zeolites, and in particular ultrastable Y (USY) modified to produce Brønsted acid sites (H-USY), represent the most promising candidates [59, 73, 87, 249]. These materials are well established in fluid catalytic cracking due to their high acidity, thermal stability, and durability, and they offer a credible foundation for adaptation to biomass conversion [250].

The central challenge is catalyst deactivation. In alcoholysis, humins and related carbonaceous residues readily accumulate on catalyst surfaces, blocking pores and deactivating acid sites. While this fouling resembles coke deposition in fluid catalytic cracking, there are important differences: fluid catalytic cracking coke generally forms as thin layers that can be reproducibly burned off, whereas humins are often particulate and strongly adhesive, making their separation and removal more problematic. In fluid catalytic cracking practice, regeneration is achieved by oxidatively combusting coke at 500–700 °C in air or oxygen, restoring activity without catastrophic loss of structure. Studies on USY regeneration during hydrocarbon cracking demonstrate that activity can be maintained across multiple cycles, though structural damage, micropore loss, and declines in acidity gradually emerge [251, 252]. More detailed investigations of industrial fluid catalytic cracking catalysts have shown that repeated regeneration alters coke morphology, producing harder carbon species that are increasingly resistant to oxidation and accelerating the degradation of zeolite crystallinity and acid site density [250]. For alcoholysis, the key unknown is whether regeneration strategies proven in fluid catalytic cracking can be reliably adapted to remove humins without compromising catalytic performance.

Beyond regeneration, humin separation poses an equally critical barrier. Unlike the thin coke layers of fluid catalytic cracking, humins form as discrete, sticky particles that are difficult to decouple from the catalyst in slurry or batch systems, leading to losses during recovery [131]. Addressing this will require new approaches, whether through catalyst design that minimises humin–catalyst contact, reactor configurations that facilitate phase separation, or humin valorisation pathways that reduce the need for separation.

The economic implications of catalyst performance are profound. Catalyst cost, turnover frequency, regeneration requirements, and separation efficiency will be among the dominant contributors to operating expenditure in alcoholysis. These parameters must therefore be explicitly integrated into techno-economic and life-cycle assessments to ensure realistic projections of process viability. Without effective regeneration protocols and reliable humin management, heterogeneous catalysis is unlikely to deliver the sustainability or cost benefits needed to displace mineral acids.

In summary, heterogeneous catalysts such as H-USY hold genuine promise for replacing H_2SO_4 , but their success will depend on resolving two critical challenges: humin separation and robust regeneration. Addressing these issues will not only enable catalyst recyclability but will also determine the economic feasibility of alcoholysis at scale, making catalyst research one of the most decisive frontiers for future work.

7.3.2 Feedstock Diversity and Model Validation

The compositional analysis presented in Chapter 4 demonstrated that the Annex IX feedstocks procured for this project, including wheat straw, miscanthus, forestry residues, and corn stover, contain not only cellulose and hemicellulose but also substantial fractions of lignin, extractives, and ash. While the present thesis has focused primarily on carbohydrate conversion pathways, future work must extend alcoholysis studies to these real feedstocks in order to capture the full influence of their additional constituents.

The effects of these fractions are significant and well documented. Lignin undergoes partial depolymerisation under acid-catalysed conditions, releasing phenolic fragments that condense with carbohydrate-derived intermediates, thereby accelerating humin polymerisation and lowering levulinate selectivity [253]. Extractives such as proteins, lipids,

and tannins introduce inhibitory interactions or secondary reaction pathways that complicate product distributions and reduce yield [254]. Ash, particularly alkali and alkaline earth metals such as potassium and calcium, neutralises Brønsted acid sites and alters catalytic environments, while silica-rich ash can contribute to pore blockage, collectively diminishing catalytic activity [195]. Experimental studies with raw lignocellulosic materials such as poplar wood confirm that under many conditions, the formation of solid residues equals or exceeds levulinic acid yields, underscoring the decisive role of feedstock composition [255].

Because compositional variability drives marked changes in product selectivity and humin burden, it provides an ideal test of the surrogate kinetic modelling framework introduced in this thesis. Built on hierarchical learning and molecular group additivity principles, the framework is inherently transferable, representing reaction pathways in terms of functional groups rather than fixed substrates. Validating this framework against the diverse feedstocks characterised in Chapter 4, with varied cellulose-to-hemicellulose ratios, lignin loads, and mineral contents, will test its predictive accuracy under industrially relevant conditions and confirm its generalisability beyond model carbohydrates.

Such validation has direct implications for process design and assessment. By linking feedstock composition to product distributions, co-product streams, and humin formation, the surrogate model can be embedded into techno-economic analysis and life-cycle assessment frameworks. Without such multi-feedstock validation, projections based on simplified substrates risk overstating achievable yields and underestimating costs, particularly for high-lignin or high-ash residues. Embedding realistic feedstock complexity into predictive modelling is therefore essential for generating robust economic and environmental projections.

In summary, extending alcoholysis studies to the diverse feedstocks analysed in Chapter 4 is not merely an incremental step. It is the essential bridge between controlled laboratory studies and industrial application, ensuring that kinetic models and economic projections reflect the true complexity of biomass. Establishing alcoholysis performance across these feedstocks will provide the necessary foundation for scaling the process into commercial biorefinery contexts and will be addressed in subsequent Ph.D. studies.

7.3.3 Process Engineering and Scale-Up

The laboratory studies presented in this thesis have demonstrated alcoholysis pathways under controlled batch conditions, but commercial deployment will require substantial advances in reactor engineering, process integration, and scale-up strategies. A central outcome of this work is the demonstration that alcoholysis reactions can be operated to true steady-state, thereby confirming maximum achievable yields of levulinates and co-products. In contrast, most prior studies have reported yields at arbitrary reaction times without distinguishing between kinetic and equilibrium phases [256]. Sustaining steady-state under continuous operation will therefore be an essential milestone for industrial viability.

Catalyst recovery and humin management represent immediate engineering priorities. In batch systems, humins remain dispersed with solid catalysts, complicating separation and recycling. Continuous-flow systems offer new opportunities: immobilising catalysts on structured supports such as packed beds, monoliths, or catalytic membranes can minimise humin fouling, while hydrocyclones, filtration units, or ceramic membranes can assist in recovering suspended catalysts. Parallel efforts in humin valorisation, including their use as precursors for carbon foams, resins, or aromatic hydrocarbons, could offset catalyst replacement costs and reduce waste burdens [131, 197]. Addressing both recovery and valorisation is therefore central to improving process economics.

Downstream processing and blending compatibility must also be optimised. Although ternary blends of levulinates, ethers, and alcohols may function directly as drop-in fuels, compliance with regulatory standards such as EN 228 (petrol) and EN 590 (diesel) will impose limits on blending and purity. Wiseman et. al. (2023) [40] has already shown that diesel blends containing up to 25% alkyl levulinate can be combusted in compression-ignition engines without modification, providing a practical benchmark for industrial feasibility. In addition to diesel and petrol, the potential to blend alkyl levulinates with marine fuel oil represents an equally important opportunity, as shipping is one of the hardest sectors to decarbonise and has fewer near-term alternatives to liquid fuels. Ensuring consistent product quality while controlling operating costs will be crucial for compliance with such standards.

The feasibility of scaling biomass conversion technologies has already been demonstrated in related contexts. For example, the iH2® process (Shell, Bangalore) operates

at demonstration scale with a 5 tonne/day capacity for agricultural residues and municipal waste, while pilot-scale pyrolysis reactors have achieved continuous biomass throughputs of 25 kg/h, producing bio-oil at high yield [257, 258]. The piloting and demonstration facilities at NREL further illustrate the availability of infrastructure for bridging laboratory chemistry with process engineering [259]. These precedents underscore that the challenge is not scale-up feasibility itself, but tailoring reactor design and integration to the unique chemistry of alcoholysis.

Achieving commercial readiness will require robust process intensification. Modular reactor designs, improved catalyst stability under regeneration, and efficient heat integration, for example, coupling alcoholysis units with upstream biomass pretreatment or downstream upgrading, will be essential to reduce energy inputs. Integrating these advances with the surrogate kinetic modelling framework developed in this thesis will enable conditions to be optimised for yield, energy efficiency, catalyst longevity, and downstream compatibility.

In addition to reactor and process considerations, the industrial deployment of alcoholysis-derived fuels will depend on meeting fuel quality specifications. Water content must be explicitly controlled due to its influence on calorific value, storage stability, and blending behaviour with diesel, as water is a known contributor to phase instability and microbial contamination in fuel storage systems [260]. Where sulphuric acid is employed as a catalyst, sulphur carry-over into product streams must be monitored and managed to ensure compliance with ultra-low sulphur diesel requirements and compatibility with modern exhaust after-treatment systems, which are sensitive to sulphur exposure [261]. Storage stability represents a further deployment constraint, as oxygenated fuel components are more susceptible to oxidative degradation during prolonged storage, potentially leading to increased acidity, viscosity changes, and deposit formation [262]. These fuel-level considerations complement the process engineering challenges discussed above and highlight that commercial readiness requires not only scalable reactor design, but also demonstrable compliance with established fuel quality and storage requirements.

In summary, scaling alcoholysis from batch studies to continuous operation depends on resolving interconnected challenges of steady-state operation, catalyst recovery, humin valorisation, blending compatibility, and downstream integration. With lessons drawn from other biomass technologies that have successfully reached pilot and demonstration scale, alcoholysis can progress from a promising laboratory process to a competitive platform for

producing sustainable fuels, positioning it as a candidate to displace a share of fossil-derived transport fuels in targeted markets.

7.3.4 Techno-Economic and Life-Cycle Assessment

7.3.4.1 Energy, Heat, and Refinement Penalties in Alcoholysis

While the experimental and modelling work presented in this thesis demonstrates the technical feasibility of alcoholysis for producing alkyl levulinate and associated co-products, industrial deployment would necessarily incur additional energy, carbon, and cost penalties that are not captured by laboratory-scale yield metrics alone. These penalties arise primarily from heat input, reactant usage, and downstream refinement requirements, which are well established as dominant cost contributors in biomass conversion processes [263, 264].

Alcoholysis reactions operate at elevated temperatures and, under batch conditions, require extended residence times to reach steady-state. At scale, supplying this thermal energy represents a significant operating cost and contributes directly to the carbon intensity of the process unless low-carbon or waste heat sources are available. While continuous operation can reduce inefficiencies associated with repeated heating and cooling, it does not eliminate the fundamental heat demand imposed by the reaction chemistry [264].

The process further relies on excess alcohol as both solvent and reactant, alongside acid catalysts and subsequent neutralisation agents. Recovery of alcohol via distillation is inherently energy-intensive, and incomplete solvent recovery increases both operating expenditure and upstream environmental burdens associated with alcohol production, as consistently highlighted in techno-economic assessments of lignocellulosic biofuel pathways [263, 265].

Downstream refinement introduces additional penalties. Separation of complex product mixtures, removal of water, neutralisation of residual acidity, and handling of salt-containing waste streams require multiple unit operations that contribute substantially to total energy demand and capital cost. More generally, downstream separations are widely recognised as one of the largest contributors to cost and energy consumption in chemical and biofuel processes [266, 267].

From a life-cycle perspective, these combined heat, reactant, and separation requirements strongly influence both operating costs and greenhouse gas emissions. Their ultimate impact depends on the degree of heat integration, solvent recovery efficiency, and the carbon intensity of energy inputs. Consequently, while alcoholysis offers promising yields and feedstock flexibility, its commercial and environmental performance must be evaluated within an integrated techno-economic and life-cycle framework rather than on conversion efficiency alone.

7.3.4.2 Implications for Techno-Economic Assessment

The commercialisation of alcoholysis will ultimately be determined not by laboratory yields alone but by its economic viability, making techno-economic assessment an essential tool for evaluating the competitiveness of the process relative to fossil fuels and other advanced biofuel pathways. Techno-economic analysis and life-cycle assessment are therefore indispensable tools for evaluating the competitiveness of the process relative to fossil fuels and other advanced biofuel pathways.

Although this thesis has not conducted techno-economic or life-cycle studies directly, the surrogate kinetic modelling framework developed here provides a robust foundation for such assessments. By linking feedstock composition, reaction pathways, and steady-state yields to downstream processing and product distributions, the model can generate quantitative inputs that are more representative of industrial conditions than conventional yield assumptions. Combined with the biochemical and elemental characterisation of RED II/RED III Annex IX feedstocks presented in Chapter 4, these outputs provide the necessary data for scenario analyses in which variations in lignin, extractives, and ash contents are systematically explored. This in turn can inform techno-economic assessments of conversion efficiency, humin formation, and separation costs, as well as life-cycle evaluations of greenhouse gas mitigation.

The integration of these contributions is already being advanced through the Sustainable Liquid Advanced Biofuels from Biomass (SusLABB) project. This programme spans feedstock preparation, process optimisation, property testing, engine trials, emissions profiling, and system-level techno-economic and life-cycle assessment. The work of this thesis aligns primarily with Work Package 1 (feedstock preparation and characterisation)

and Work Package 2 (fuel production), while complementary packages extend to downstream testing and assessment. By providing mechanistic and modelling insights, this thesis delivers the data backbone for those subsequent benchmarking activities.

Preliminary findings from techno-economic assessments conducted within SusLABB suggest that humin valorisation and solvent recovery will be critical to offset operating expenditure, while catalyst recyclability and energy integration strongly influence both economic and environmental performance. These themes mirror broader analyses of biofuel deployment, where sensitivity studies consistently highlight feedstock costs, catalyst lifetimes, and downstream separations as decisive factors [268].

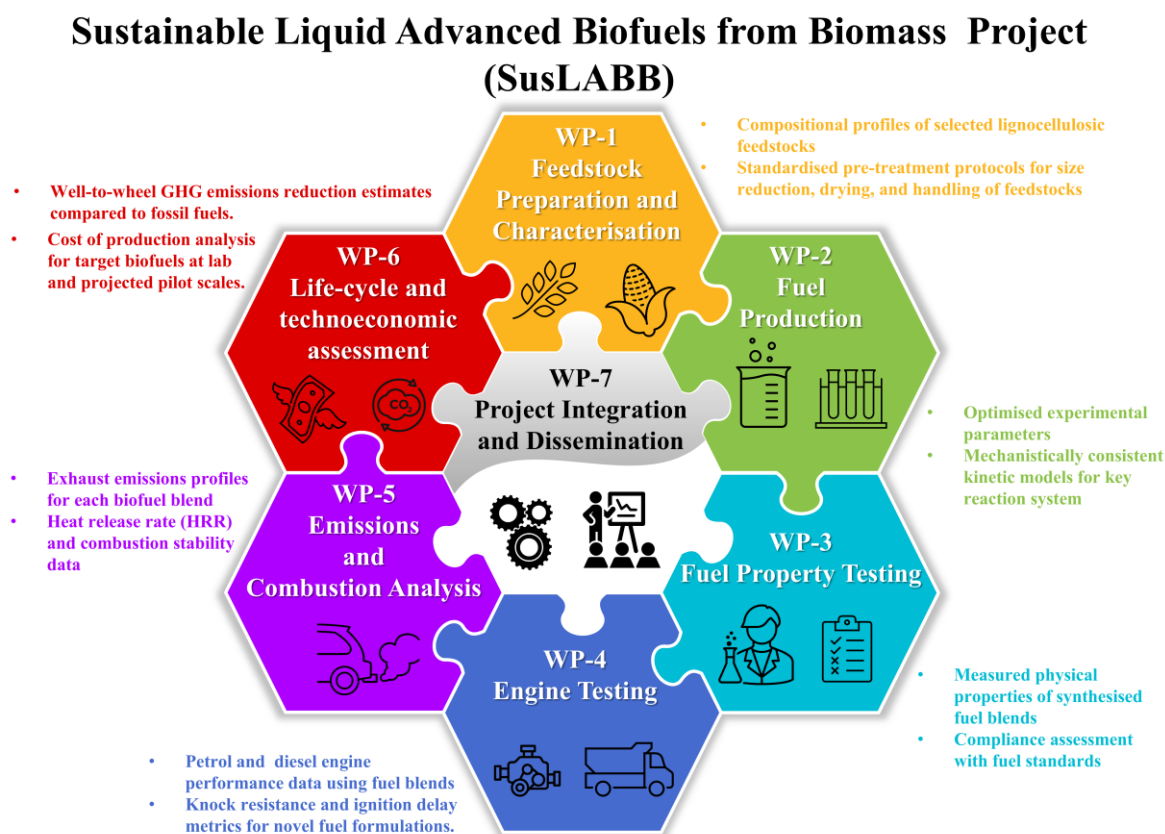


Figure 53. Schematic overview of the Sustainable Liquid Advanced Biofuels from Biomass (SusLABB) project, illustrating the seven interconnected work packages (WP1–WP7). The project spans feedstock preparation and characterisation through to fuel production, testing, emissions analysis, and techno-economic assessment. Work packages most directly addressed in this thesis are WP1 and WP2.

7.3.4.3 Implications for Life-Cycle Assessment

Life-cycle assessment will be equally important for positioning alcoholysis within wider energy and climate strategies, as it captures the greenhouse gas implications of feedstock sourcing, conversion energy, and end-use emissions across the full fuel life-cycle. Alkyl levulinates offer the potential to displace fossil fuels in hard-to-abate sectors, particularly heavy-duty transport and marine shipping, due to their favourable blending properties and compatibility with existing engines [40]. A well-to-wheel perspective is required, encompassing feedstock production, conversion, and end-use emissions. Incorporating humin valorisation and renewable solvent recovery within the system boundary could significantly reduce greenhouse gas intensity compared to fossil diesel and first-generation biofuels. Comparative studies of advanced pathways such as hydrotreated vegetable oils and Fischer–Tropsch fuels have reported reductions of 50–80 percent [269], underscoring the importance of benchmarking alcoholysis against established alternatives to identify its niche contribution.

In summary, techno-economic and life-cycle assessment are not peripheral considerations but essential to advancing alcoholysis towards deployment. While these assessments fall outside the scope of this thesis, the experimental and modelling advances presented here provide the data required for their realistic implementation. Embedding alcoholysis within such integrated frameworks will be decisive in determining its viability as a scalable and sustainable platform for advanced biofuels.

7.3.5 Emissions and Combustion Analysis

The deployment of alcoholysis-derived alkyl levulinates ultimately depends on their combustion behaviour and emissions performance. While these aspects were outside the scope of this thesis, they are critical for regulatory approval and practical implementation. As previously demonstrated [40], diesel blends containing up to 25% butyl levulinate maintained stable engine operation without modification and achieved significant reductions in particulate emissions, providing an important proof of concept for end-use viability.

Early results from ongoing SusLABB trials are beginning to provide further insights. Drive cycle testing of butyl levulinate blends in diesel engines indicates that vehicle

driveability remains unchanged, with significant reductions in particulate and carbon monoxide emissions relative to fossil diesel. These benefits, however, were accompanied by a modest increase in fuel consumption and elevated NO_x emissions, highlighting the need for systematic follow-up testing under WP4 and WP5 of SusLABB.

These trade-offs are not unique to alkyl levulinates. Similar patterns have been observed with other oxygenated biofuels such as biodiesel and furanics, where reductions in soot and CO were offset by variable impacts on NO_x [270, 271]. This reinforces that the observed behaviour of levulinates is consistent with broader experience in oxygenated fuel combustion.

In summary, while preliminary evidence highlights the promise of alkyl levulinates as clean-burning blending components, comprehensive and systematic engine testing remains essential. Such studies will not only provide robust emissions data for regulatory assessment but will also support integration with the surrogate modelling framework developed in this thesis. This will enable predictive links between feedstock composition, process optimisation, and real-world engine performance. Their high oxygen content and blending compatibility position alkyl levulinates as particularly promising candidates for reducing particulate emissions in hard-to-abate transport sectors, especially heavy-duty vehicles and marine shipping.

7.4 Overall Outlook

This thesis has demonstrated that alcoholysis is a feasible and strategically relevant pathway for producing alkyl levulinates from lignocellulosic biomass. It established steady-state yield analysis as a methodological benchmark for the field, enabling performance to be assessed at true equilibrium rather than at transient maxima. It also revealed, for the first time, that both cellulose and hemicellulose contribute to levulinate formation, and introduced a yield representation framework that captures these dual contributions. In parallel, a surrogate kinetic modelling approach was developed that can be generalised across diverse feedstocks, while new experimental insights were gained into acid consumption and secondary co-product formation during biomass conversion. Taken together, these contributions advance alcoholysis beyond conventional yield reporting, establishing

methodological standards, providing mechanistic insight, and delivering predictive tools to guide process optimisation across the wider field of biomass conversion.

Looking ahead, three interlinked priorities define the future of alcoholysis research. First, catalyst innovation is essential: while homogeneous acids have enabled laboratory-scale breakthroughs, their corrosivity and waste generation limit industrial scalability. Recyclable heterogeneous systems such as modified zeolites, particularly those resistant to humin fouling, offer a pathway to sustainable operation. Second, process integration and co-product valorisation will be central to economic viability. Persistent by-products such as humins could be upgraded into carbon materials, resins, or aromatics, transforming them from a disposal burden into a revenue stream and improving life-cycle performance. Third, model-driven optimisation must remain at the core of development. The surrogate and hierarchical modelling concepts introduced here provide a transferable framework for representing biomass complexity and predicting product distributions, but need to be validated across a diverse range of feedstocks, such as those listed in Chapter 4. By coupling this approach to reactor engineering, scale-up, and sustainability assessments, alcoholysis can be tailored not only for yield but also for desired techno-economic and environmental outcomes.

Ultimately, the significance of alcoholysis lies in its potential contribution to the decarbonisation of hard-to-abate transport sectors. Alkyl levulicates combine favourable blending properties with the capacity to reduce soot emissions, positioning them as valuable components in advanced biofuel blends. Developed in parallel with other sustainable pathways such as hydrotreated vegetable oils and Fischer–Tropsch fuels, alcoholysis can diversify the portfolio of renewable transport fuels and reduce the risks of over-reliance on any single technology.

In conclusion, the advances presented in this thesis provide a foundation for the next generation of alcoholysis research, combining experimental insight, modelling innovation, and interdisciplinary collaboration. By integrating process development with techno-economic, life-cycle, and end-use considerations, alcoholysis can progress from a promising laboratory process to a competitive industrial platform. In doing so, it not only offers a route to sustainable fuel supply but also contributes to the broader transformation of biomass utilisation into a resilient and circular bioeconomy [272, 273].

Bibliography

- [1] U.N.F.C.o.C. Change, Paris Agreement, United Nations, Paris, 2015.
- [2] H. Ritchie, Rosado, P., & Roser, M., Breakdown of carbon dioxide, methane and nitrous oxide emissions by sector, 2021.
- [3] M. Sharmina, O.Y. Edelenbosch, C. Wilson, R. Freeman, D.E.H.J. Gernaat, P. Gilbert, A. Larkin, E.W. Littleton, M. Traut, D.P. Van Vuuren, N.E. Vaughan, F.R. Wood, C. Le Quéré, Decarbonising the critical sectors of aviation, shipping, road freight and industry to limit warming to 1.5–2°C, *Climate Policy* 21 (2021) 455-474.
- [4] I.A.G. Wilson, P. Styring, Why Synthetic Fuels Are Necessary in Future Energy Systems, *Frontiers in Energy Research* 5 (2017).
- [5] E.A.S.A.C. (EASAC), Decarbonisation of Transport: Options and Challenges, EASAC, Halle, Germany, 2019.
- [6] F. Alanazi, Electric Vehicles: Benefits, Challenges, and Potential Solutions for Widespread Adaptation, *Applied Sciences* 13 (2023) 6016.
- [7] A.F. Pennington, C.R. Cornwell, K.D. Sircar, M.C. Mirabelli, Electric vehicles and health: A scoping review, *Environ Res* 251 (2024) 118697.
- [8] U.S.E.P.A. (EPA), "Electric Vehicle Myths", U.S. Environmental Protection Agency, 2023.
- [9] M.C. Portal, "Are Electric Vehicles Definitely Better for the Climate than Gas-Powered Cars?", Massachusetts Institute of Technology (MIT), 2023.
- [10] L.A.-W. Ellingsen, B. Singh, A.H. Strømman, The size and range effect: lifecycle greenhouse gas emissions of electric vehicles, *Environmental Research Letters* 11 (2016) 054010.
- [11] J.B. Dunn, L. Gaines, J. Sullivan, M.Q. Wang, Impact of Recycling on Cradle-to-Gate Energy Consumption and Greenhouse Gas Emissions of Automotive Lithium-Ion Batteries, *Environmental Science & Technology* 46 (2012) 12704-12710.
- [12] I.E. Agency, Global EV Outlook 2022: Securing supplies for an electric future, International Energy Agency, Paris, 2022.
- [13] G. Zubi, R. Dufo-López, M. Carvalho, G. Pasaoglu, The lithium-ion battery: State of the art and future perspectives, *Renewable and Sustainable Energy Reviews* 89 (2018) 292-308.
- [14] P. Nikolaidis, A. Poullikkas, A comparative overview of hydrogen production processes, *Renewable and Sustainable Energy Reviews* 67 (2017) 597-611.

- [15] R. Bhandari, C.A. Trudewind, P. Zapp, Life cycle assessment of hydrogen production via electrolysis – a review, *Journal of Cleaner Production* 85 (2014) 151-163.
- [16] I.E. Agency, The Future of Hydrogen: Seizing today's opportunities, International Energy Agency, Paris, 2019.
- [17] I. Staffell, D. Scamman, A. Velazquez Abad, P. Balcombe, P.E. Dodds, P. Ekins, N. Shah, K.R. Ward, The role of hydrogen and fuel cells in the global energy system, *Energy & Environmental Science* 12 (2019) 463-491.
- [18] A. Mehmeti, A. Angelis-Dimakis, G. Arampatzis, S. McPhail, S. Ulgiati, Life Cycle Assessment and Water Footprint of Hydrogen Production Methods: From Conventional to Emerging Technologies, *Environments* 5 (2018) 24.
- [19] J. Hansson, S. Brynolf, E. Fridell, M. Lehtveer, The Potential Role of Ammonia as Marine Fuel—Based on Energy Systems Modeling and Multi-Criteria Decision Analysis, *Sustainability* 12 (2020) 3265.
- [20] D. Banister, The sustainable mobility paradigm, *Transport Policy* 15 (2008) 73-80.
- [21] F. Creutzig, P. Jochem, O.Y. Edelenbosch, L. Mattauch, D.P.V. Vuuren, D. McCollum, J. Minx, Transport: A roadblock to climate change mitigation?, *Science* 350 (2015) 911-912.
- [22] T. Searchinger, R. Heimlich, R.A. Houghton, F. Dong, A. Elobeid, J. Fabiosa, S. Tokgoz, D. Hayes, T.-H. Yu, Use of U.S. Croplands for Biofuels Increases Greenhouse Gases Through Emissions from Land-Use Change, *Science* 319 (2008) 1238-1240.
- [23] F. Cherubini, A.H. Strømman, Life cycle assessment of bioenergy systems: State of the art and future challenges, *Bioresource Technology* 102 (2011) 437-451.
- [24] S. Jablonski, N. Strachan, C. Brand, A. Bauen, The role of bioenergy in the UK's energy future formulation and modelling of long-term UK bioenergy scenarios, *Energy Policy* 38 (2010) 5799-5816.
- [25] C. Chuck, Biofuels for aviation: feedstocks, technology and implementation, Academic Press 2016.
- [26] C.O. Tuck, E. Pérez, I.T. Horváth, R.A. Sheldon, M. Poliakoff, Valorization of Biomass: Deriving More Value from Waste, *Science* 337 (2012) 695-699.
- [27] Directive (EU) 2018/2001 of the European Parliament and of the Council of 11 December 2018 on the promotion of the use of energy from renewable sources., 2018.
- [28] E.P.a. Council, Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources, 2009.
- [29] E.P.a. Council, Directive (EU) 2023/2413 of the European Parliament and of the Council of 18 October 2023 on the promotion of the use of energy from renewable sources (recast), 2023.
- [30] C.a.C. Department of the Environment, Climate Action Plan 2024, Government of Ireland, Dublin, 2024.
- [31] D.B. Sulis, N. Lavoine, H. Sederoff, X. Jiang, B.M. Marques, K. Lan, C. Cofre-Vega, R. Barrangou, J.P. Wang, Advances in lignocellulosic feedstocks for bioenergy and bioproducts, *Nature Communications* 16 (2025) 1244.
- [32] A. Taghizadeh-Alisaraei, A. Tatari, M. Khanali, M. Keshavarzi, Potential of biofuels production from wheat straw biomass, current achievements and perspectives: a review, *Biofuels* 14 (2023) 79-92.

- [33] N. Scarlat, J.-F. Dallemand, F. Monforti-Ferrario, V. Nita, The role of biomass and bioenergy in a future bioeconomy: Policies and facts, *Environmental Development* 15 (2015) 3-34.
- [34] D. Styles, M.B. Jones, Energy crops in Ireland: Quantifying the potential life-cycle greenhouse gas reductions of energy-crop electricity, *Biomass and Bioenergy* 31 (2007) 759-772.
- [35] A. Démolis, N. Essayem, F. Rataboul, Synthesis and Applications of Alkyl Levulinate, *ACS Sustainable Chemistry & Engineering* 2 (2014) 1338-1352.
- [36] Y. Hishikawa, M. Yamaguchi, S. Kubo, T. Yamada, Direct preparation of butyl levulinate by a single solvolysis process of cellulose, *Journal of wood science* 59 (2013) 179-182.
- [37] J.F. Leal Silva, R. Grekin, A.P. Mariano, R. Maciel Filho, Making Levulinic Acid and Ethyl Levulinate Economically Viable: A Worldwide Technoeconomic and Environmental Assessment of Possible Routes, *Energy Technology* 6 (2018) 613-639.
- [38] J.P. Lange, Lignocellulose conversion: an introduction to chemistry, process and economics, *Biofuels, Bioproducts and Biorefining: Innovation for a sustainable economy* 1 (2007) 39-48.
- [39] M.J. Climent, A. Corma, S. Iborra, Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels, *Green Chemistry* 16 (2014) 516.
- [40] S. Wiseman, Properties and Performance of Model Lignocellulose Derived Biofuel Mixtures as Low Carbon Replacements for Diesel Fuels, *School of Chemical and Process Engineering, University of Leeds, Leeds, UK*, 2023.
- [41] S. Wiseman, C.A. Michelbach, H. Li, A.S. Tomlin, Predicting the physical properties of three-component lignocellulose derived advanced biofuel blends using a design of experiments approach, *Sustainable Energy & Fuels* 7 (2023) 5283-5300.
- [42] C. Michelbach, K. Hakimov, A. Farooq, A.S. Tomlin, Predicting the autoignition behaviour of tailorable advanced biofuel blends using automatically generated mechanisms, *Proceedings of the Combustion Institute* 40 (2024) 105667.
- [43] M.A. Nahil, O. Aboelazayem, S. Wiseman, N. Herar, V. Dupont, A. Alazzawi, A.S. Tomlin, A.B. Ross, Production and Optimisation of Oxygenated Biofuel Blend Components via the Ethanolysis of Lignocellulosic Biomass: A Response Surface Methodology, *Energies* 18 (2025) 2985.
- [44] C. McNamara, A. O'Shea, P. Rao, A. Ure, L. Ayarde-Henríquez, M.R. Ghaani, A. Ross, S. Dooley, Steady states and kinetic modelling of the acid-catalysed ethanolysis of glucose, cellulose, and corn cob to ethyl levulinate, *Energy Advances* (2024).
- [45] A. Démolis, N. Essayem, F. Rataboul, Synthesis and Applications of Alkyl Levulinate, *ACS Sustainable Chemistry & Engineering* 2 (2014) 1338-1352.
- [46] M. Mascal, E.B. Nikitin, Comment on Processes for the Direct Conversion of Cellulose or Cellulosic Biomass into Levulinate Esters, *ChemSusChem* 3 (2010) 1349-1351.
- [47] W. Zhu, C. Chang, C. Ma, F. Du, Kinetics of Glucose Ethanolysis Catalyzed by Extremely Low Sulfuric Acid in Ethanol Medium, *Chinese Journal of Chemical Engineering* 22 (2014) 238-242.

- [48] N. Shi, Q. Liu, H. Cen, R. Ju, X. He, L. Ma, Formation of humins during degradation of carbohydrates and furfural derivatives in various solvents, *Biomass Conversion and Biorefinery* 10 (2020) 277-287.
- [49] X. Hu, C. Lievens, A. Larcher, C.-Z. Li, Reaction pathways of glucose during esterification: Effects of reaction parameters on the formation of humin type polymers, *Bioresource Technology* 102 (2011) 10104-10113.
- [50] C. Ming, K. Sun, Y. Shao, Z. Zhang, S. Zhang, Q. Liu, Y. Wang, S. Hu, J. Xiang, X. Hu, Conversion of Cellulose to Levulinic Acid/Ester over an Acid Catalyst: Impacts of Dispersion of Hydrogen Ions on Polymerization Reactions, *Energy & Fuels* 33 (2019) 11187-11199.
- [51] M.S.Í. Howard, Real Reaction Kinetics for the Production and Utilisation of Advanced Biofuels, Department of Chemical Sciences, University of Limerick, 2019.
- [52] S. Wang, Y. Chen, Y. Jia, G. Xu, C. Chang, Q. Guo, H. Tao, C. Zou, K. Li, Experimental and theoretical studies on glucose conversion in ethanol solution to 5-ethoxymethylfurfural and ethyl levulinate catalyzed by a Brønsted acid, *Physical Chemistry Chemical Physics* 23 (2021) 19729-19739.
- [53] B. Xiang, Y. Wang, T. Qi, H.-Q. Yang, C.-W. Hu, Promotion catalytic role of ethanol on Brønsted acid for the sequential dehydration-etherification of fructose to 5-ethoxymethylfurfural, *Journal of Catalysis* 352 (2017) 586-598.
- [54] M. Pointner, P. Kuttner, T. Obrlik, A. Jager, H. Kahr, Composition of corncobs as a substrate for fermentation of biofuels, *Agronomy Research* 12 (2014) 391-396.
- [55] M. Kelly, M. Fortune, G. Bourque, S. Dooley, Machine learned compact kinetic models for methane combustion, *Combustion and Flame* 253 (2023) 112755.
- [56] Y. Zhang, C. Liu, X. Chen, Mechanism of glucose conversion in supercritical water by DFT study, *Journal of Analytical and Applied Pyrolysis* 119 (2016) 199-207.
- [57] M.K. Ghosh, M.S. Howard, K. Dussan, S. Dooley, Mechanism and theory of d-glucopyranose homogeneous acid catalysis in the aqueous solution phase, *Physical Chemistry Chemical Physics* 21 (2019) 17993-18011.
- [58] J.R. Bernardo, M.C. Oliveira, A.C. Fernandes, HReO₄ as highly efficient and selective catalyst for the conversion of carbohydrates into value added chemicals, *Molecular Catalysis* 465 (2019) 87-94.
- [59] X. Song, J. Yue, Y. Zhu, C. Wen, L. Chen, Q. Liu, L. Ma, C. Wang, Efficient Conversion of Glucose to 5-Hydroxymethylfurfural over a Sn-Modified SAPO-34 Zeolite Catalyst, *Industrial & Engineering Chemistry Research* 60 (2021) 5838-5851.
- [60] G. Qiu, C. Huang, X. Sun, B. Chen, Highly active niobium-loaded montmorillonite catalysts for the production of 5-hydroxymethylfurfural from glucose, *Green Chemistry* 21 (2019) 3930-3939.
- [61] T. Flannelly, S. Dooley, J.J. Leahy, Reaction Pathway Analysis of Ethyl Levulinate and 5-Ethoxymethylfurfural from <sc>d</sc>-Fructose Acid Hydrolysis in Ethanol, *Energy & Fuels* 29 (2015) 7554-7565.
- [62] E. Ahmad, M.I. Alam, K.K. Pant, M.A. Haider, Catalytic and mechanistic insights into the production of ethyl levulinate from biorenewable feedstocks, *Green Chemistry* 18 (2016) 4804-4823.

- [63] A. Beckendorff, A. Lamp, M. Kaltschmitt, Optimization of hydrolysis conditions for xylans and straw hydrolysates by HPLC analysis, *Biomass Conversion and Biorefinery* 13 (2023) 3361-3374.
- [64] E. Amis, *Solvent effects on chemical phenomena*, Elsevier 2012.
- [65] K. Laidler, *Chemical Kinetics*, (Harper and Row, New York, 1987), b) AA Frost, RG Pearson, *Kinetics and Mechanism*, second ed., Wiley, New York (1988) 88.
- [66] A.M. Raspolli Galletti, C. Antonetti, S. Fulignati, D. Licursi, Direct Alcoholysis of Carbohydrate Precursors and Real Cellulosic Biomasses to Alkyl Levulinates: A Critical Review, *Catalysts* 10 (2020) 1221.
- [67] A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, *Biomass and Bioenergy* 38 (2012) 68-94.
- [68] G. Xu, B. Chen, Z. Zheng, K. Li, H. Tao, One-pot ethanolysis of carbohydrates to promising biofuels: 5-ethoxymethylfurfural and ethyl levulinate, *Asia-Pacific Journal of Chemical Engineering* 12 (2017) 527-535.
- [69] G.-Z. Xu, C. Chang, W.-N. Zhu, B. Li, X.-J. Ma, F.-G. Du, A comparative study on direct production of ethyl levulinate from glucose in ethanol media catalysed by different acid catalysts, *Chemical Papers* 67 (2013) 1355-1363.
- [70] M. Bosilj, J. Schmidt, A. Fischer, R.J. White, One pot conversion of glucose to ethyl levulinate over a porous hydrothermal acid catalyst in green solvents, *RSC Advances* 9 (2019) 20341-20344.
- [71] K. Sun, L. Zhang, Y. Shao, Q. Li, H. Fan, G. Gao, S. Zhang, Q. Liu, Y. Wang, X. Hu, Conversion of monosaccharides into levulinic acid/esters: impacts of metal sulfate addition and the reaction medium, *Journal of Chemical Technology & Biotechnology* 94 (2019) 3676-3686.
- [72] F. Yu, R. Zhong, H. Chong, M. Smet, W. Dehaen, B.F. Sels, Fast catalytic conversion of recalcitrant cellulose into alkyl levulinates and levulinic acid in the presence of soluble and recoverable sulfonated hyperbranched poly(arylene oxindole)s, *Green Chemistry* 19 (2017) 153-163.
- [73] C. Chang, G. Xu, W. Zhu, J. Bai, S. Fang, One-pot production of a liquid biofuel candidate—Ethyl levulinate from glucose and furfural residues using a combination of extremely low sulfuric acid and zeolite USY, *Fuel* 140 (2015) 365-370.
- [74] J. Chen, G. Zhao, L. Chen, Efficient production of 5-hydroxymethylfurfural and alkyl levulinate from biomass carbohydrate using ionic liquid-based polyoxometalate salts, *RSC Advances* 4 (2014) 4194-4202.
- [75] J. Gu, J. Zhang, D. Li, H. Yuan, Y. Chen, Hyper-cross-linked polymer based carbonaceous materials as efficient catalysts for ethyl levulinate production from carbohydrates, *Journal of Chemical Technology & Biotechnology* 94 (2019) 3073-3083.
- [76] D. Gupta, C. Mukesh, K.K. Pant, Topotactic transformation of homogeneous phosphotungstomolybdic acid materials to heterogeneous solid acid catalyst for carbohydrate conversion to alkyl methylfurfural and alkyl levulinate, *RSC Advances* 10 (2020) 705-718.
- [77] E.Y.C. Jorge, C.G.S. Lima, T.M. Lima, L. Marchini, M.B. Gawande, O. Tomanec, R.S. Varma, M.W. Paixão, Sulfonated dendritic mesoporous silica nanospheres: a metal-free

- Lewis acid catalyst for the upgrading of carbohydrates, *Green Chemistry* 22 (2020) 1754-1762.
- [78] G. Morales, A. Osatiashtiani, B. Hernández, J. Iglesias, J.A. Melero, M. Paniagua, D. Robert Brown, M. Granollers, A.F. Lee, K. Wilson, Conformal sulfated zirconia monolayer catalysts for the one-pot synthesis of ethyl levulinate from glucose, *Chemical Communications* 50 (2014) 11742-11745.
- [79] N. Mulik, P. Niphadkar, V. Bokade, Synergetic combination of H₂Zr₁PW₁₂O₄₀ and Sn-Beta as potential solid acid catalyst for direct one-step transformation of glucose to ethyl levulinate, a biofuel additive, *Environmental Progress & Sustainable Energy* 38 (2019) 13173.
- [80] L. Peng, L. Lin, J. Zhang, J. Shi, S. Liu, Solid acid catalyzed glucose conversion to ethyl levulinate, *Applied Catalysis A: General* 397 (2011) 259-265.
- [81] S. Saravanamurugan, A. Riisager, Zeolite Catalyzed Transformation of Carbohydrates to Alkyl Levulinates, *ChemCatChem* 5 (2013) 1754-1757.
- [82] D. Song, Q. Zhang, Y. Sun, P. Zhang, Y.-H. Guo, J.-L. Hu, Design of Ordered Mesoporous Sulfonic Acid Functionalized ZrO₂/organosilica Bifunctional Catalysts for Direct Catalytic Conversion of Glucose to Ethyl Levulinate, *ChemCatChem* 10 (2018) 4953-4965.
- [83] J. Zhang, J. Chen, Modified solid acids derived from biomass based cellulose for one-step conversion of carbohydrates into ethyl levulinate, *Journal of Energy Chemistry* 25 (2016) 747-753.
- [84] Z. Zhang, H. Yuan, An alumina-coated UiO-66 nanocrystalline solid superacid with high acid density as a catalyst for ethyl levulinate synthesis, *Journal of Chemical Technology & Biotechnology* 95 (2020) 2930-2942.
- [85] S. Zhao, G. Xu, C. Chang, S. Fang, Z. Liu, F. Du, Direct Conversion of Carbohydrates into Ethyl Levulinate with Potassium Phosphotungstate as an Efficient Catalyst, *Catalysts* 5 (2015) 1897-1910.
- [86] S. Zhao, G. Xu, J. Chang, C. Chang, J. Bai, S. Fang, Z. Liu, Direct Production of Ethyl Levulinate from Carbohydrates Catalyzed by H-ZSM-5 Supported Phosphotungstic Acid, *2015 10* (2015) 12.
- [87] J. Heda, P. Niphadkar, V. Bokade, Efficient Synergetic Combination of H-USY and SnO₂ for Direct Conversion of Glucose into Ethyl Levulinate (Biofuel Additive), *Energy & Fuels* 33 (2019) 2319-2327.
- [88] S.R. B, K.K. P, D.L. D, L. N, One pot selective transformation of biomass derived chemicals towards alkyl levulinates over titanium exchanged heteropoly tungstate catalysts, *Catalysis Today* 309 (2018) 269-275.
- [89] Z. Babaei, A. Najafi Chermahini, M. Dinari, Alumina-coated mesoporous silica SBA-15 as a solid catalyst for catalytic conversion of fructose into liquid biofuel candidate ethyl levulinate, *Chemical Engineering Journal* 352 (2018) 45-52.
- [90] C.-H. Kuo, A.S. Poyraz, L. Jin, Y. Meng, L. Pahalagedara, S.-Y. Chen, D.A. Kriz, C. Guild, A. Gudz, S.L. Suib, Heterogeneous acidic TiO₂ nanoparticles for efficient conversion of biomass derived carbohydrates, *Green Chemistry* 16 (2014) 785-791.
- [91] H. Liu, X. Chen, Y. Zhang, M. Lu, H. Lyu, L. Han, W. Xiao, Alcoholysis of Ball-Milled Corn Stover: The Enhanced Conversion of Carbohydrates into Biobased Chemicals over

Combination Catalysts of [Bmim-SO₃H][HSO₄] and Al₂(SO₄)₃, *Energy & Fuels* 34 (2020) 7085-7093.

[92] P.F. Pinheiro, D.M. Chaves, M.J. da Silva, One-pot synthesis of alkyl levulinates from biomass derivative carbohydrates in tin(II) exchanged silicotungstates-catalyzed reactions, *Cellulose* 26 (2019) 7953-7969.

[93] S. Quereschi, E. Ahmad, K.K.K. Pant, S. Dutta, Insights into Microwave-Assisted Synthesis of 5-Ethoxymethylfurfural and Ethyl Levulinate Using Tungsten Disulfide as a Catalyst, *ACS Sustainable Chemistry & Engineering* 8 (2020) 1721-1729.

[94] S. Saravanamurugan, O. Nguyen Van Buu, A. Riisager, Conversion of Mono- and Disaccharides to Ethyl Levulinate and Ethyl Pyranoside with Sulfonic Acid-Functionalized Ionic Liquids, *ChemSusChem* 4 (2011) 723-726.

[95] L. Zhang, Y. Zhu, L. Tian, Y. He, H. Wang, F. Deng, One-pot alcoholysis of carbohydrates to biofuel 5-ethoxymethylfurfural and 5-methoxymethylfurfural via a sulfonic porous polymer, *Fuel Processing Technology* 193 (2019) 39-47.

[96] F. Chengjiang, L. Yan, Y. Zhaozhuo, L. Hu, Y. Song, Efficient Catalytic Upgrade of Fructose to Alkyl Levulinates with Phenylpyridine- phosphotungstate Solid Hybrids, *Current Green Chemistry* 6 (2019) 44-52.

[97] D.P. Serrano, J.A. Melero, G. Morales, J. Iglesias, P. Pizarro, Progress in the design of zeolite catalysts for biomass conversion into biofuels and bio-based chemicals, *Catalysis Reviews* 60 (2018) 1-70.

[98] S. Karnjanakom, P. Maneechakr, C. Samart, S. Kongparakul, G. Guan, A. Bayu, Direct conversion of sugar into ethyl levulinate catalyzed by selective heterogeneous acid under co-solvent system, *Catalysis Communications* 143 (2020) 106058.

[99] A.S. Amarasekara, B. Wiredu, Acidic Ionic Liquid Catalyzed One-Pot Conversion of Cellulose to Ethyl Levulinate and Levulinic Acid in Ethanol-Water Solvent System, *BioEnergy Research* 7 (2014) 1237-1243.

[100] I. Bodachivskyi, U. Kuzhiumparambil, D.B.G. Williams, Metal triflates are tunable acidic catalysts for high yielding conversion of cellulosic biomass into ethyl levulinate, *Fuel Processing Technology* 195 (2019) 106159.

[101] W. Deng, M. Liu, Q. Zhang, Y. Wang, Direct transformation of cellulose into methyl and ethyl glucosides in methanol and ethanol media catalyzed by heteropolyacids, *Catalysis Today* 164 (2011) 461-466.

[102] Y.-B. Huang, T. Yang, Y.-T. Lin, Y.-Z. Zhu, L.-C. Li, H. Pan, Facile and high-yield synthesis of methyl levulinate from cellulose, *Green Chemistry* 20 (2018) 1323-1334.

[103] C. Song, S. Liu, X. Peng, J. Long, W. Lou, X. Li, Catalytic Conversion of Carbohydrates to Levulinate Ester over Heteropolyanion-Based Ionic Liquids, *ChemSusChem* 9 (2016) 3307-3316.

[104] G. Xu, C. Chang, S. Fang, X. Ma, Cellulose reactivity in ethanol at elevated temperature and the kinetics of one-pot preparation of ethyl levulinate from cellulose, *Renewable Energy* 78 (2015) 583-589.

[105] L. Zhou, D. Gao, J. Yang, X. Yang, Y. Su, T. Lu, Conversion of recalcitrant cellulose to alkyl levulinates and levulinic acid via oxidation pretreatment combined with alcoholysis over Al₂(SO₄)₃, *Cellulose* 27 (2020) 1451-1463.

- [106] C. Chang, G. Xu, X. Jiang, Production of ethyl levulinate by direct conversion of wheat straw in ethanol media, *Bioresource Technology* 121 (2012) 93-99.
- [107] L. di Bitonto, G. Antonopoulou, C. Braguglia, C. Campanale, A. Gallipoli, G. Lyberatos, I. Ntaikou, C. Pastore, Lewis-Brønsted acid catalysed ethanolysis of the organic fraction of municipal solid waste for efficient production of biofuels, *Bioresource Technology* 266 (2018) 297-305.
- [108] C. Gong, J. Wei, X. Tang, X. Zeng, Y. Sun, L. Lin, Production of levulinic acid and ethyl levulinate from cellulosic pulp derived from the cooking of lignocellulosic biomass with active oxygen and solid alkali, *Korean Journal of Chemical Engineering* 36 (2019) 740-752.
- [109] Q. Guan, T. Lei, Z. Wang, H. Xu, L. Lin, G. Chen, X. Li, Z. Li, Preparation of ethyl levulinate from wheat straw catalysed by sulfonate ionic liquid, *Industrial Crops and Products* 113 (2018) 150-156.
- [110] T.-H. Kim, Y.-K. Oh, J.W. Lee, Y.K. Chang, Levulinate production from algal cell hydrolysis using in situ transesterification, *Algal Research* 26 (2017) 431-435.
- [111] R. Le Van Mao, Q. Zhao, G. Dima, D. Petraccone, New Process for the Acid-Catalyzed Conversion of Cellulosic Biomass (AC3B) into Alkyl Levulinates and Other Esters Using a Unique One-Pot System of Reaction and Product Extraction, *Catalysis Letters* 141 (2011) 271-276.
- [112] H. Liu, Y. Zhang, T. Hou, X. Chen, C. Gao, L. Han, W. Xiao, Mechanical deconstruction of corn stover as an entry process to facilitate the microwave-assisted production of ethyl levulinate, *Fuel Processing Technology* 174 (2018) 53-60.
- [113] J. Tan, Q. Liu, L. Chen, T. Wang, L. Ma, G. Chen, Efficient production of ethyl levulinate from cassava over $\text{Al}_2(\text{SO}_4)_3$ catalyst in ethanol–water system, *Journal of Energy Chemistry* 26 (2017) 115-120.
- [114] Y.W. Tiong, C.L. Yap, S. Gan, W.S.P. Yap, One-pot conversion of oil palm empty fruit bunch and mesocarp fiber biomass to levulinic acid and upgrading to ethyl levulinate via indium trichloride-ionic liquids, *Journal of Cleaner Production* 168 (2017) 1251-1261.
- [115] J. Yang, J. Park, J. Son, B. Kim, J.W. Lee, Enhanced ethyl levulinate production from citrus peels through an in-situ hydrothermal reaction, *Bioresource Technology Reports* 2 (2018) 84-87.
- [116] Y. Zhang, X. Wang, T. Hou, H. Liu, L. Han, W. Xiao, Efficient microwave-assisted production of biofuel ethyl levulinate from corn stover in ethanol medium, *Journal of Energy Chemistry* 27 (2018) 890-897.
- [117] T. Zhao, Y. Zhang, G. Zhao, X. Chen, L. Han, W. Xiao, Impact of biomass feedstock variability on acid-catalyzed alcoholysis performance, *Fuel Processing Technology* 180 (2018) 14-22.
- [118] W. Zhao, Y. Li, C. Song, S. Liu, X. Li, J. Long, Intensified levulinic acid/ester production from cassava by one-pot cascade prehydrolysis and delignification, *Applied Energy* 204 (2017) 1094-1100.
- [119] P.T. Anastas, J.C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, 2000.

- [120] C. Antonetti, S. Gori, D. Licursi, G. Pasini, S. Frigo, M. López, J.C. Parajó, A.M. Raspolli Galletti, One-pot alcoholysis of the lignocellulosic *Eucalyptus nitens* biomass to n-butyl levulinate, a valuable additive for diesel motor fuel, *Catalysts* 10 (2020) 509.
- [121] A.M. Raspolli Galletti, D. Licursi, S. Ciorba, N. Di Fidio, V. Coccia, F. Cotana, C. Antonetti, Sustainable exploitation of residual *Cynara cardunculus* L. to levulinic acid and n-butyl levulinate, *Catalysts* 11 (2021) 1082.
- [122] M.S. Howard, G. Issayev, N. Naser, S.M. Sarathy, A. Farooq, S. Dooley, Ethanolic gasoline, a lignocellulosic advanced biofuel, *Sustainable Energy & Fuels* 3 (2019) 409-421.
- [123] A.M.R. Galletti, C. Antonetti, V. De Luise, D. Licursi, N. NASSI O DI NASSO, Levulinic acid production from waste biomass, *BioResources* 7 (2012) 1824-1834.
- [124] A. O'Shea, C. McNamara, P. Rao, M. Howard, M.R. Ghanni, S. Dooley, A hierarchical surrogate approach to biomass ethanolysis reaction kinetic modelling, *Reaction Chemistry & Engineering* (2025).
- [125] L. Zhang, L. Tian, Z. Xu, L. Wang, Direct production of ethyl levulinate from carbohydrates and biomass waste catalyzed by modified porous silica with multiple acid sites, *Process Biochemistry* 121 (2022) 152-162.
- [126] X. Kang, Y.-Y. Wang, S. Wang, X. Song, Xylan and xylose decomposition during hot water pre-extraction: A pH-regulated hydrolysis, *Carbohydrate Polymers* 255 (2021) 117391.
- [127] J.R. Martins, J.H.R. Llanos, M.M. Abe, M.L. Costa, M. Brienzo, New blend of renewable bioplastic based on starch and acetylated xylan with high resistance to oil and water vapor, *Carbohydrate Research* 537 (2024) 109068.
- [128] M. Tyufekchiev, K. Ralph, P. Duan, S. Yuan, K. Schmidt-Rohr, M.T. Timko, Rapid Depolymerization of Decrystallized Cellulose to Soluble Products via Ethanolysis under Mild Conditions, *ChemSusChem* 13 (2020) 2634-2641.
- [129] Y. Wang, L. Li, X. Zou, R. Shu, L. Ding, K. Yao, W. Lv, G. Liu, Impact of Humin on Soil Adsorption and Remediation of Cd(II), Pb(II), and Cu(II), *Soil and Sediment Contamination: An International Journal* 25 (2016) 700-715.
- [130] S. Ge, W. Jiang, L. Zheng, X. Xie, Y. Pan, Green remediation of high-lead contaminated soil by stabilization/solidification with insoluble humin: Long-term leaching and mechanical characteristics, *Journal of Cleaner Production* 324 (2021) 129184.
- [131] E. De Jong, M. Mascal, S. Constant, T. Claessen, P. Tosi, A. Mija, The origin, composition, and applications of industrial humins – a review, *Green Chemistry* 27 (2025) 3136-3166.
- [132] D.M. Pham, H. Oji, S. Yagi, S. Ogawa, A. Katayama, Sulfur in humin as a redox-active element for extracellular electron transfer, *Geoderma* 408 (2022) 115580.
- [133] S. Wang, Y. Chen, Y. Jia, C. Wang, G. Xu, Y. Jiao, C. He, C. Chang, Q. Guo, DFT and dynamic analysis of glucose alcoholysis conversion to 5-ethoxymethylfurfural and ethyl levulinate, *Fuel* 326 (2022) 125075.
- [134] C. Ming, K. Sun, Y. Shao, Z. Zhang, S. Zhang, Q. Liu, Y. Wang, S. Hu, J. Xiang, X. Hu, Conversion of Cellulose to Levulinic Acid/Ester over an Acid Catalyst: Impacts of Dispersion of Hydrogen Ions on Polymerization Reactions, *Energy & Fuels* 33 (2019) 11187-11199.

- [135] E.S. Olson, M.R. Kjelden, A.J. Schlag, R.K. Sharma, Levulinate Esters from Biomass Wastes, Chemicals and Materials from Renewable Resources, American Chemical Society 2001, pp. 51-63.
- [136] H. Rizquallah, J. Yang, J.W. Lee, Temperature-swing transesterification for the coproduction of biodiesel and ethyl levulinate from spent coffee grounds, *Korean Journal of Chemical Engineering* 39 (2022) 2754-2763.
- [137] K. Sun, L. Zhang, Y. Shao, Q. Li, H. Fan, G. Gao, S. Zhang, Q. Liu, Y. Wang, X. Hu, Conversion of monosaccharides into levulinic acid/esters: impacts of metal sulfate addition and the reaction medium, *Journal of Chemical Technology & Biotechnology* 94 (2019) 3676-3686.
- [138] F. Lai, F. Yan, P. Wang, F. Qu, X. Shen, Z. Zhang, Efficient one-pot synthesis of ethyl levulinate from carbohydrates catalyzed by Wells-Dawson heteropolyacid supported on Ce-Si pillared montmorillonite, *Journal of Cleaner Production* 324 (2021) 129276.
- [139] O.U. Isocyanates, *Ullmann's encyclopedia of industrial chemistry*, (1985).
- [140] H. Li, Z. Fang, S. Yang, Direct Conversion of Sugars and Ethyl Levulinate into γ -Valerolactone with Superparamagnetic Acid-Base Bifunctional ZrFeOx Nanocatalysts, *ACS Sustainable Chemistry & Engineering* 4 (2016) 236-246.
- [141] R. Liu, J. Chen, X. Huang, L. Chen, L. Ma, X. Li, Conversion of fructose into 5-hydroxymethylfurfural and alkyl levulinates catalyzed by sulfonic acid-functionalized carbon materials, *Green Chemistry* 15 (2013) 2895-2903.
- [142] J. Chen, G. Zhao, L. Chen, Efficient production of 5-hydroxymethylfurfural and alkyl levulinate from biomass carbohydrate using ionic liquid-based polyoxometalate salts, *RSC Adv.* 4 (2014) 4194-4202.
- [143] D. Di Menno Di Bucchianico, J.-C. Buvat, M. Mignot, V. Casson Moreno, S. Leveneur, Role of solvent in enhancing the production of butyl levulinate from fructose, *Fuel* 318 (2022) 123703.
- [144] E. Ramírez, R. Bringué, C. Fité, M. Iborra, J. Tejero, F. Cunill, Assessment of ion exchange resins as catalysts for the direct transformation of fructose into butyl levulinate, *Applied Catalysis A: General* 612 (2021) 117988.
- [145] R. An, G. Xu, C. Chang, J. Bai, S. Fang, Efficient one-pot synthesis of n-butyl levulinate from carbohydrates catalyzed by $\text{Fe}_2(\text{SO}_4)_3$, *Journal of Energy Chemistry* 26 (2017) 556-563.
- [146] Z. Babaei, R. Yazdanpanah Esmaeilabad, N. Orash, A. Najafi Chermahini, Sulfonated CMK-3: an effective catalyst for the glucose conversion to butyl levulinate as the fuel additive, *Biomass Conversion and Biorefinery* 13 (2023) 61-71.
- [147] M. Hao, L. Jin-Xing, W. Fu-Rong, W. Le-Fu, L. Xue-Hui, Conversion of Cellulose to Butyl Levulinate in Bio-Butanol Medium Catalyzed by Acidic Ionic Liquids, *Acta Physico-Chimica Sinica* 31 (2015) 973-979.
- [148] L. Deng, C. Chang, R. An, X. Qi, G. Xu, Metal sulfates-catalyzed butanolysis of cellulose: butyl levulinate production and optimization, *Cellulose* 24 (2017) 5403-5415.
- [149] C.-H. Kuo, A.S. Poyraz, L. Jin, Y. Meng, L. Pahalagedara, S.-Y. Chen, D.A. Kriz, C. Guild, A. Guduz, S.L. Suib, Heterogeneous acidic TiO_2 nanoparticles for efficient conversion of biomass derived carbohydrates, *Green Chemistry* 16 (2014) 785.

- [150] Z. Babaei, A. Najafi Chermahini, M. Dinari, Synthesis of n-butyl levulinate as a fuel additive using bimetallic Zr/Al catalysts supported on mesoporous silica: Applying experimental design to optimize the reaction conditions, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 625 (2021) 126885.
- [151] A.M. Raspolli Galletti, R. Lorè, D. Licursi, N. Di Fidio, C. Antonetti, S. Fulignati, Insights on butyl levulinate bio-blendstock: From model sugars to paper mill waste cellulose as feedstocks for a sustainable catalytic butanolysis process, *Catalysis Today* 418 (2023) 114054.
- [152] B. Hahn-Hägerdal, K. Karhumaa, C. Fonseca, I. Spencer-Martins, M.F. Gorwa-Grauslund, Towards industrial pentose-fermenting yeast strains, *Applied microbiology and biotechnology* 74 (2007) 937-953.
- [153] D.C. Elliott, P. Biller, A.B. Ross, A.J. Schmidt, S.B. Jones, Hydrothermal liquefaction of biomass: Developments from batch to continuous process, *Bioresource Technology* 178 (2015) 147-156.
- [154] P. Weiland, Biogas production: current state and perspectives, *Applied Microbiology and Biotechnology* 85 (2010) 849-860.
- [155] B. Yang, C.E. Wyman, Pretreatment: the key to unlocking low-cost cellulosic ethanol, *Biofuels, Bioproducts and Biorefining: Innovation for a sustainable economy* 2 (2008) 26-40.
- [156] C. Liu, X. Lu, Z. Yu, J. Xiong, H. Bai, R. Zhang, Production of levulinic acid from cellulose and cellulosic biomass in different catalytic systems, *Catalysts* 10 (2020) 1006.
- [157] L.C. Meher, D.V. Sagar, S.N. Naik, Technical aspects of biodiesel production by transesterification—a review, *Renewable and sustainable energy reviews* 10 (2006) 248-268.
- [158] L.A. Mannion, A. Bell, T. Watson-Murphy, M. Kelly, M.R. Ghaani, S. Dooley, A physics constrained methodology for the life cycle assessment of sustainable aviation fuel production, *Biomass and Bioenergy* 185 (2024) 107169.
- [159] M. Ostadi, E. Rytter, M. Hillestad, Boosting carbon efficiency of the biomass to liquid process with hydrogen from power: The effect of H₂/CO ratio to the Fischer-Tropsch reactors on the production and power consumption, *Biomass and Bioenergy* 127 (2019) 105282.
- [160] E. Ranzi, M. Dente, A. Goldaniga, G. Bozzano, T. Faravelli, Lumping procedures in detailed kinetic modeling of gasification, pyrolysis, partial oxidation and combustion of hydrocarbon mixtures, *Progress in Energy and Combustion Science* 27 (2001) 99-139.
- [161] D. Mohan, C.U. Pittman Jr, P.H. Steele, Pyrolysis of wood/biomass for bio-oil: a critical review, *Energy & fuels* 20 (2006) 848-889.
- [162] P. Basu, *Biomass gasification and pyrolysis: practical design and theory*, Academic press 2010.
- [163] M. Puig-Arnavat, J.C. Bruno, A. Coronas, Review and analysis of biomass gasification models, *Renewable and sustainable energy reviews* 14 (2010) 2841-2851.
- [164] A. Demirbas, Combustion characteristics of different biomass fuels, *Progress in energy and combustion science* 30 (2004) 219-230.

- [165] P. McKendry, Energy production from biomass (part 1): overview of biomass. bioresource technology, 83 (1), 37—46, 2002.
- [166] A.A. Peterson, F. Vogel, R.P. Lachance, M. Fröling, M.J. Antal Jr, J.W. Tester, Thermochemical biofuel production in hydrothermal media: a review of sub-and supercritical water technologies, Energy & environmental science 1 (2008) 32-65.
- [167] P. Biller, A. Ross, Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content, Bioresource technology 102 (2011) 215-225.
- [168] L.R. Lynd, M.S. Laser, D. Bransby, B.E. Dale, B. Davison, R. Hamilton, M. Himmel, M. Keller, J.D. McMillan, J. Sheehan, C.E. Wyman, How biotech can transform biofuels, Nature Biotechnology 26 (2008) 169-172.
- [169] E. Palmqvist, B. Hahn-Hägerdal, Fermentation of lignocellulosic hydrolysates. I: inhibition and detoxification, Bioresource technology 74 (2000) 17-24.
- [170] I. Angelidaki, L. Treu, P. Tsapekos, G. Luo, S. Campanaro, H. Wenzel, P.G. Kougias, Biogas upgrading and utilization: Current status and perspectives, Biotechnology advances 36 (2018) 452-466.
- [171] C. Holliger, M. Alves, D. Andrade, I. Angelidaki, S. Astals, U. Baier, C. Bougrier, P. Buffière, M. Carballa, V. De Wilde, Towards a standardization of biomethane potential tests, Water Science and Technology 74 (2016) 2515-2522.
- [172] B. Yang, Z. Dai, S.-Y. Ding, C.E. Wyman, Enzymatic hydrolysis of cellulosic biomass, Biofuels 2 (2011) 421-450.
- [173] M.E. Himmel, S.-Y. Ding, D.K. Johnson, W.S. Adney, M.R. Nimlos, J.W. Brady, T.D. Foust, Biomass recalcitrance: engineering plants and enzymes for biofuels production, science 315 (2007) 804-807.
- [174] V.B. Borugadda, V.V. Goud, Biodiesel production from renewable feedstocks: Status and opportunities, Renewable and Sustainable Energy Reviews 16 (2012) 4763-4784.
- [175] S.A. Akhade, N. Singh, O.Y. Gutiérrez, J. Lopez-Ruiz, H. Wang, J.D. Holladay, Y. Liu, A. Karkamkar, R.S. Weber, A.B. Padmaperuma, Electrocatalytic hydrogenation of biomass-derived organics: a review, Chemical reviews 120 (2020) 11370-11419.
- [176] J.P. Lange, E. Van Der Heide, J. van Buijtenen, R. Price, Furfural—a promising platform for lignocellulosic biofuels, ChemSusChem 5 (2012) 150-166.
- [177] K. Yan, Y. Yang, J. Chai, Y. Lu, Catalytic reactions of gamma-valerolactone: A platform to fuels and value-added chemicals, Applied Catalysis B: Environmental 179 (2015) 292-304.
- [178] R. Aguilar, J.A. Ramírez, G. Garrote, M. Vázquez, Kinetic study of the acid hydrolysis of sugar cane bagasse, Journal of Food Engineering 55 (2002) 309-318.
- [179] J.K. Saini, R. Saini, L. Tewari, Lignocellulosic agriculture wastes as biomass feedstocks for second-generation bioethanol production: concepts and recent developments, 3 Biotech 5 (2015) 337-353.
- [180] A. Pugazhendhi, T. Mathimani, S. Varjani, E.R. Rene, G. Kumar, S.-H. Kim, V.K. Ponnusamy, J.-J. Yoon, Biobutanol as a promising liquid fuel for the future - recent updates and perspectives, Fuel 253 (2019) 637-646.

- [181] F. Xin, C. Wang, W. Dong, W. Zhang, H. Wu, J. Ma, M. Jiang, Comprehensive investigations of biobutanol production by a non-acetone and 1,3-propanediol generating *Clostridium* strain from glycerol and polysaccharides, *Biotechnology for Biofuels* 9 (2016).
- [182] A. Sluiter, Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., & Crocker, D., Determination of Structural Carbohydrates and Lignin in Biomass, National Renewable Energy Laboratory (NREL), 2012.
- [183] M.L. Sinnott, Catalytic mechanism of enzymic glycosyl transfer, *Chemical Reviews* 90 (1990) 1171-1202.
- [184] A.C. Puișel, G.D. Suditu, M. Danu, G.-L. Ailiesei, M.T. Nechita, An experimental study on the hot alkali extraction of xylan-based hemicelluloses from wheat straw and corn stalks and optimization methods, *Polymers* 14 (2022) 1662.
- [185] X. Zhou, W. Li, R. Mabon, L.J. Broadbelt, A mechanistic model of fast pyrolysis of hemicellulose, *Energy & Environmental Science* 11 (2018) 1240-1260.
- [186] J. Zhang, T. Chen, J. Wu, J. Wu, A novel Gaussian-DAEM-reaction model for the pyrolysis of cellulose, hemicellulose and lignin, *RSC Advances* 4 (2014) 17513.
- [187] E. Ranzi, A. Cuoci, T. Faravelli, A. Frassoldati, G. Migliavacca, S. Pierucci, S. Sommariva, Chemical Kinetics of Biomass Pyrolysis, *Energy & Fuels* 22 (2008) 4292-4300.
- [188] M. Frei, Lignin: Characterization of a Multifaceted Crop Component, *The Scientific World Journal* 2013 (2013) 1-25.
- [189] J.M. Desmarchelier, F.M. Johnston, L.T. Vu, Ethyl formate, formic acid and ethanol in air, wheat, barley and sultanas: analysis of natural levels and fumigant residues, *Pesticide Science* 55 (1999) 815-824.
- [190] S. Kang, G. Zhang, Q. Yang, J. Tu, X. Guo, F. Qin, Y. Xu, A New Technology for Utilization of Biomass Hydrolysis Residual Humins for Acetic Acid Production, *BioResources* 11 (2016).
- [191] F. Jin, Z. Zhou, A. Kishita, H. Enomoto, Hydrothermal conversion of biomass into acetic acid, *Journal of Materials Science* 41 (2006) 1495-1500.
- [192] M. Choura, N.M. Belgacem, A. Gandini, Acid-Catalyzed Polycondensation of Furfuryl Alcohol: Mechanisms of Chromophore Formation and Cross-Linking, *Macromolecules* 29 (1996) 3839-3850.
- [193] X. Hu, S. Jiang, S. Kadarwati, D. Dong, C.-Z. Li, Effects of water and alcohols on the polymerization of furan during its acid-catalyzed conversion into benzofuran, *RSC Advances* 6 (2016) 40489-40501.
- [194] H. Rasmussen, H.R. Sørensen, A.S. Meyer, Formation of degradation compounds from lignocellulosic biomass in the biorefinery: sugar reaction mechanisms, *Carbohydrate Research* 385 (2014) 45-57.
- [195] R. Weingarten, J. Cho, R. Xing, W.C. Conner, G.W. Huber, Kinetics and Reaction Engineering of Levulinic Acid Production from Aqueous Glucose Solutions, *ChemSusChem* 5 (2012) 1280-1290.
- [196] S.K.R. Patil, C.R.F. Lund, Formation and Growth of Humins via Aldol Addition and Condensation during Acid-Catalyzed Conversion of 5-Hydroxymethylfurfural, *Energy & Fuels* 25 (2011) 4745-4755.

- [197] I. Van Zandvoort, Y. Wang, C.B. Rasrendra, E.R.H. Van Eck, P.C.A. Bruijninx, H.J. Heeres, B.M. Weckhuysen, Formation, Molecular Structure, and Morphology of Humins in Biomass Conversion: Influence of Feedstock and Processing Conditions, *ChemSusChem* 6 (2013) 1745-1758.
- [198] K.C. Badgujar, V.C. Badgujar, B.M. Bhanage, A review on catalytic synthesis of energy rich fuel additive levulinate compounds from biomass derived levulinic acid, *Fuel Processing Technology* 197 (2020) 106213.
- [199] B. Caslin, *Straw for Energy*, Teagasc, 2020.
- [200] Eurostat, *Agricultural production - crops*, Eurostat 2024.
- [201] A. Kärkönen, R. Korpinen, E. Järvenpää, A. Aalto, P. Saranpää, Properties of Oat and Barley Hulls and Suitability for Food Packaging Materials, *Journal of Natural Fibers* 19 (2022) 13326-13336.
- [202] I.N.a.D.F. Council, *Statistical Yearbook 2022/2023*, 2023.
- [203] P.A. Duc, P. Dharanipriya, B.K. Velmurugan, M. Shanmugavadivu, Groundnut shell -a beneficial bio-waste, *Biocatalysis and Agricultural Biotechnology* 20 (2019) 101206.
- [204] F.a.t.M. Department of Agriculture, *Forest Statistics – Ireland 2024*, in: F.a.t.M. Department of Agriculture (Ed.) Dublin, 2024.
- [205] E. Anderson, A. Rebecca, M. Matthew, O. Adebosola, W. Andrew, T. and Voigt, Growth and agronomy of *Miscanthus x giganteus* for biomass production, *Biofuels* 2 (2011) 71-87.
- [206] C. Wang, Y. Kong, R. Hu, G. Zhou, *Miscanthus*: A fast-growing crop for environmental remediation and biofuel production, *GCB Bioenergy* 13 (2021) 58-69.
- [207] T.Z. Ruan, R; Yin, X. Y; Zhang, S. X; Yang, Z. H, Water hyacinth (*Eichhornia crassipes*) biomass as a biofuel feedstock by enzymatic hydrolysis, *Bioresources* 11 (2016) 2372-2380.
- [208] A.K. Chandel, S.S. Da Silva, W. Carvalho, O.V. Singh, Sugarcane bagasse and leaves: foreseeable biomass of biofuel and bio-products, *Journal of Chemical Technology & Biotechnology* 87 (2012) 11-20.
- [209] E. Borsella, P. Colucci, G. Lembo, H. Lange, *Degradative Methods for Lignin Valorization*, *Lignin Chemistry* 2024, pp. 85-138.
- [210] Y. Liao, *A Brief Introduction of Lignin*, *Lignin Chemistry* 2024, pp. 1-13.
- [211] C.-Y. Ma, Y. Xu, L.-H. Xu, C. Zhang, J.-Y. Qi, J.-L. Wen, *NMR Characterization of Lignin*, *Lignin Chemistry* 2024, pp. 15-60.
- [212] O. Musl, A. Potthast, *Advances in the Molar Mass and Functionality Analysis of Lignin*, *Lignin Chemistry* 2024, pp. 61-83.
- [213] L.J. Jönsson, C. Martín, Pretreatment of lignocellulose: Formation of inhibitory by-products and strategies for minimizing their effects, *Bioresource Technology* 199 (2016) 103-112.
- [214] A. Lorenci Woiciechowski, C.J. Dalmas Neto, L. Porto de Souza Vandenberghe, D.P. de Carvalho Neto, A.C. Novak Sydney, L.A.J. Letti, S.G. Karp, L.A. Zevallos Torres, C.R. Soccol, Lignocellulosic biomass: Acid and alkaline pretreatments and their effects on biomass recalcitrance – Conventional processing and recent advances, *Bioresource Technology* 304 (2020) 122848.

- [215] A.H. Sluiter, B.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D.; Crocker, D., Determination of Structural Carbohydrates and Lignin in Biomass: Laboratory Analytical Procedure (LAP); Technical Report NREL/TP-510-42618, National Renewable Energy Laboratory, Golden, Colorado, 2012.
- [216] R. Chopda, J.A. Ferreira, M.J. Taherzadeh, Biorefining Oat Husks into High-Quality Lignin and Enzymatically Digestible Cellulose with Acid-Catalyzed Ethanol Organosolv Pretreatment, *Processes* 8 (2020) 435.
- [217] IEA, Tracking Transport 2020, IEA, Paris, 2020, pp. <https://www.iea.org/reports/tracking-transport-2020>.
- [218] Y.-K. Oh, K.-R. Hwang, C. Kim, J.R. Kim, J.-S. Lee, Recent developments and key barriers to advanced biofuels: A short review, *Bioresource Technology* 257 (2018) 320-333.
- [219] J. Witcover, R.B. Williams, Comparison of “Advanced” biofuel cost estimates: Trends during rollout of low carbon fuel policies, *Transportation Research Part D: Transport and Environment* 79 (2020) 102211.
- [220] Y. Sun, J. Cheng, Hydrolysis of lignocellulosic materials for ethanol production: a review, *Bioresource Technology* 83 (2002) 1-11.
- [221] F.-X. Collard, J. Blin, A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin, *Renewable and Sustainable Energy Reviews* 38 (2014) 594-608.
- [222] A. Molino, V. Larocca, S. Chianese, D. Musmarra, Biofuels Production by Biomass Gasification: A Review, *Energies* 11 (2018) 811.
- [223] J.A. Ramirez, R.J. Brown, T.J. Rainey, A Review of Hydrothermal Liquefaction Bio-Crude Properties and Prospects for Upgrading to Transportation Fuels, *Energies* 8 (2015) 6765-6794.
- [224] T. Wang, Y. Zhai, Y. Zhu, C. Li, G. Zeng, A review of the hydrothermal carbonization of biomass waste for hydrochar formation: Process conditions, fundamentals, and physicochemical properties, *Renewable and Sustainable Energy Reviews* 90 (2018) 223-247.
- [225] E. Christensen, A. Williams, S. Paul, S. Burton, R.L. McCormick, Properties and performance of levulinate esters as diesel blend components, *Energy & Fuels* 25 (2011) 5422-5428.
- [226] C.L. Williams, T.L. Westover, R.M. Emerson, J.S. Tumuluru, C. Li, Sources of Biomass Feedstock Variability and the Potential Impact on Biofuels Production, *BioEnergy Research* 9 (2016) 1-14.
- [227] T.A. Semelsberger, R.L. Borup, H.L. Greene, Dimethyl ether (DME) as an alternative fuel, *Journal of Power Sources* 156 (2006) 497-511.
- [228] K. Oehlenschläger, J.-N. Hengsbach, M. Volkmar, R. Ulber, From pre-culture to solvent: current trends in *Clostridium acetobutylicum* cultivation, *Applied Microbiology and Biotechnology* 109 (2025).
- [229] M. Li, W. Li, Q. Liu, H. Jameel, H.-m. Chang, S. An, L. Ma, A two-step conversion of corn stover into furfural and levulinic acid in a water/gamma-valerolactone system, *BioResources* 11 (2016) 8239-8256.

- [230] S. Alipour, H. Omidvarborna, High concentration levulinic acid production from corn stover, *RSC Advances* 6 (2016) 111616-111621.
- [231] H. Liu, H. Meng, H. Cong, X. Shen, X. Chen, H. Xing, J. Dai, Alcoholysis kinetics and mechanism studies of ethyl levulinate production from ball milled corn stover, *RSC Advances* 12 (2022) 34145-34153.
- [232] H. Zhang, Y.-T. Cheng, T.P. Vispute, R. Xiao, G.W. Huber, Catalytic conversion of biomass-derived feedstocks into olefins and aromatics with ZSM-5: the hydrogen to carbon effective ratio, *Energy & Environmental Science* 4 (2011) 2297.
- [233] A. Wolny, D. Więclawik, J. Zdarta, S. Jurczyk, T. Jesionowski, A. Chrobok, Robust biocatalyst for the green continuous flow synthesis of esters from biomass-derived furfuryl alcohol and C8–C18 carboxylic acids, *Green Chemistry* 26 (2024) 10829-10841.
- [234] P. Pietrek, M. Kraut, R. Dittmeyer, Towards a Novel Computer-Aided Optimization of Microreactors: Techno-Economic Evaluation of an Immobilized Enzyme System, *Symmetry* 13 (2021) 524.
- [235] W.-Y. Yang, H.-D. Zhang, J.-Y. Hu, Z.-P. Zhao, L. Sang, Intensified Synthesis of Levulinic Acid from Fructose over Solid Acid Catalysts in Micropacked Bed Reactors, *Industrial & Engineering Chemistry Research* 63 (2024) 22390-22402.
- [236] A. Démolis, M. Eternot, N. Essayem, F. Rataboul, Influence of butanol isomers on the reactivity of cellulose towards the synthesis of butyl levulinates catalyzed by liquid and solid acid catalysts, *New Journal of Chemistry* 40 (2016) 3747-3754.
- [237] A. Jaswal, P.P. Singh, T. Mondal, Furfural—a versatile, biomass-derived platform chemical for the production of renewable chemicals, *Green Chemistry* 24 (2022) 510-551.
- [238] A. Pundir, M. Singh Thakur, S. Prakash, N. Kumari, N. Sharma, Z. He, S. Nam, S. Dhumal, K. Sharma, S. Saxena, S. Kumar, S.V. Deshmukh, M. Kumar, Furfural as a low-volume, high-value asset from agricultural residues: A review on production, agricultural applications and environmental sustainability, *Heliyon* 10 (2024) e35077.
- [239] A. Tripodi, M. Belotti, I. Rossetti, Bioethylene Production: From Reaction Kinetics to Plant Design, *ACS Sustainable Chemistry & Engineering* 7 (2019) 13333-13350.
- [240] N.A. Aali, G.J. Hadi, Kinetic Study of Ethanol Dehydration to Ethylene and Diethyl Ether in Catalytic Packed Bed Reactor Over ZSM-5 Catalyst, (2023).
- [241] T. Kim, R.S. Assary, H. Kim, C.L. Marshall, D.J. Gosztola, L.A. Curtiss, P.C. Stair, Effects of solvent on the furfuryl alcohol polymerization reaction: UV Raman spectroscopy study, *Catalysis Today* 205 (2013) 60-66.
- [242] Y. Lv, Y. Jiang, J. Lu, H. Gao, W. Dong, J. Zhou, W. Zhang, F. Xin, M. Jiang, Comprehensive evaluation for the one-pot biosynthesis of butyl acetate by using microbial mono- and co-cultures, *Biotechnology for Biofuels* 14 (2021).
- [243] A.A. Al-Rabiah, A.E. Alqahtani, R.K. Al Darwish, A.S. Bin Naqyah, Novel Process for Butyl Acetate Production via Membrane Reactor: A Comparative Study with the Conventional and Reactive Distillation Processes, *Processes* 10 (2022) 1801.
- [244] S. Vranckx, J. Beeckmann, W. Kopp, C. Lee, L. Cai, H. Chakravarty, H. Olivier, K. Leonhard, H. Pitsch, R. Fernandes, An experimental and kinetic modelling study of n-butyl formate combustion, *Combustion and Flame* 160 (2013) 2680–2692.
- [245] N.C.f.B. Information, Butyl Formate, PubChem, National Library of Medicine, 2025.

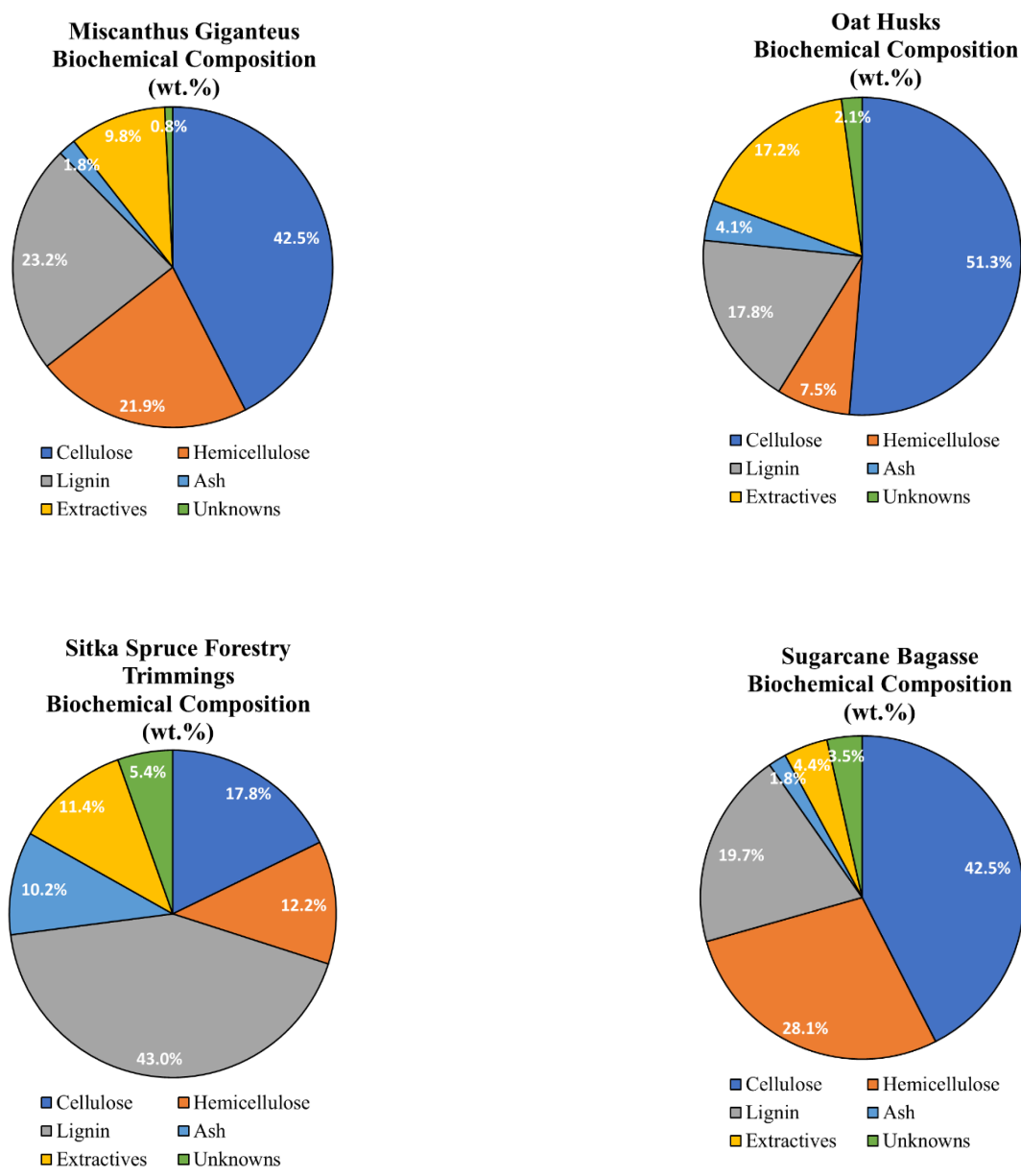
- [246] Y. Wang, W. Liu, L. Zhang, Q. Hou, Characterization and comparison of lignin derived from corncob residues to better understand its potential applications, *International Journal of Biological Macromolecules* 134 (2019) 20-27.
- [247] W.-Y. Yang, R.-X. Zhang, X.-F. Zheng, Z.-P. Zhao, L. Sang, Highly-efficient synthesis of 5-Hydroxymethylfurfural from fructose in micropacked bed Reactors: Multiphase Transport, reaction Optimization, and heterogeneous kinetic study, *Chemical Engineering Journal* 497 (2024) 154863.
- [248] L. Zhang, J. Yue, Packed Bed Microreactors for Sustainable Chemistry and Process Development, *Chemistry* 7 (2025) 29.
- [249] Z. Zheng, C. Wang, Y. Chen, S. Wang, Q. Guo, C. Chang, H. Tao, G. Xu, One-pot efficient conversion of glucose into biofuel 5-ethoxymethylfurfural catalyzed by zeolite solid catalyst, *Biomass Conversion and Biorefinery* 13 (2023) 8927-8938.
- [250] Q. Almas, M.A. Naeem, M.A.S. Baldanza, J. Solomon, J.C. Kenvin, C.R. Müller, V. Teixeira da Silva, C.W. Jones, C. Sievers, Transformations of FCC catalysts and carbonaceous deposits during repeated reaction-regeneration cycles, *Catalysis Science & Technology* 9 (2019) 6977-6992.
- [251] C. Kassargy, S. Awad, G. Burnens, G. Upreti, K. Kahine, M. Tazerout, Study of the effects of regeneration of USY zeolite on the catalytic cracking of polyethylene, *Applied Catalysis B: Environmental* 244 (2019) 704-708.
- [252] L. Wei, H. Wang, Q. Dong, Y. Li, H. Xiang, A Review on the Research Progress of Zeolite Catalysts for Heavy Oil Cracking, *Catalysts* 15 (2025) 401.
- [253] G. Hurst, A. Teklemariam, S. Brierley, M.A. Diaz De Rienzo, S. Tedesco, Lignocellulosic biomass conversion to levulinic acid via acid catalysis: Current methods, opportunities and challenges for self-sustaining biorefineries, *International Journal of Thermofluids* 27 (2025) 101175.
- [254] W.O.D. Darryn W Rackemann, The conversion of lignocellulosics to levulinic acid, Society of Chemical Industry and John Wiley & Sons, Ltd (2011).
- [255] G. Hurst, I. Brangeli, M. Peeters, S. Tedesco, Solid residue and by-product yields from acid-catalysed conversion of poplar wood to levulinic acid, *Chemical Papers* 74 (2020) 1647-1661.
- [256] B. Girisuta, L. Janssen, H. Heeres, A kinetic study on the decomposition of 5-hydroxymethylfurfural into levulinic acid, *Green Chemistry* 8 (2006) 701-709.
- [257] E.B.C.a.E. (EUBCE), Booklet on Biomass Conversion Technologies: Pilot and Demonstration Plants in Europe and Worldwide, 2021.
- [258] W. Jerzak, E. Acha, B. Li, Comprehensive Review of Biomass Pyrolysis: Conventional and Advanced Technologies, Reactor Designs, Product Compositions and Yields, and Techno-Economic Analysis, *Energies* 17 (2024) 5082.
- [259] N.R.E. Laboratory, Scale-Up and Piloting Research for Biomass Conversion Technologies, 2024.
- [260] B.R. Moser, Biodiesel production, properties, and feedstocks, *In Vitro Cellular & Developmental Biology - Plant* 45 (2009) 229-266.
- [261] O. van Rheinberg, K. Lucka, H. Köhne, T. Schade, J.T. Andersson, Selective removal of sulphur in liquid fuels for fuel cell applications, *Fuel* 87 (2008) 2988-2996.

- [262] K. Bacha, A. Ben-Amara, A. Vannier, M. Alves-Fortunato, M. Nardin, Oxidation stability of diesel/biodiesel fuels measured by a PetroOxy device and characterization of oxidation products, *Energy & Fuels* 29 (2015) 4345-4355.
- [263] E. Gnansounou, A. Dauriat, Techno-economic analysis of lignocellulosic ethanol: a review, *Bioresource technology* 101 (2010) 4980-4991.
- [264] S. Jones, P. Meyer, L. Snowden-Swan, A. Padmaperuma, E. Tan, A. Dutta, J. Jacobson, K. Cafferty, Process design and economics for the conversion of lignocellulosic biomass to hydrocarbon fuels: fast pyrolysis and hydrotreating bio-oil pathway, National Renewable Energy Lab.(NREL), Golden, CO (United States), 2013.
- [265] D. Humbird, Process design and economics for biochemical conversion of lignocellulosic biomass to ethanol, Technical Report (2011) 40-43.
- [266] W.D. Seider, D.R. Lewin, J. Seader, S. Widagdo, R. Gani, K.M. Ng, Product and process design principles: synthesis, analysis and evaluation, John Wiley & Sons 2016.
- [267] K.D. Timmerhaus, R.E. West, Plant design and economics for chemical engineers, McGraw-Hill 2004.
- [268] G. Sorda, M. Banse, C. Kemfert, An overview of biofuel policies across the world, *Energy policy* 38 (2010) 6977-6988.
- [269] F. Liu, M. Shafique, X. Luo, Literature review on life cycle assessment of transportation alternative fuels, *Environmental Technology & Innovation* 32 (2023) 103343.
- [270] M. Lapuerta, O. Armas, J. Rodríguez-Fernández, Effect of biodiesel fuels on diesel engine emissions, *Progress in Energy and Combustion Science* 34 (2008) 198-223.
- [271] J. Frost, P. Hellier, N. Ladommatos, A systematic study into the effect of lignocellulose-derived biofuels on the combustion and emissions of fossil diesel blends in a compression ignition engine, *Fuel* 313 (2022) 122663.
- [272] O.A. Marzouk, Summary of the 2023 report of TCEP (tracking clean energy progress) by the International Energy Agency (IEA), and proposed process for computing a single aggregate rating, E3S Web of Conferences, EDP Sciences, 2025, pp. 00048.
- [273] V. Fernández Ocamica, M. Bernardes Figueirêdo, S. Zapata, C. Bartolomé, Assessment of EU Bio-Based Economy Sectors Based on Environmental, Socioeconomic, and Technical Indicators, *Sustainability* 16 (2024) 1971.

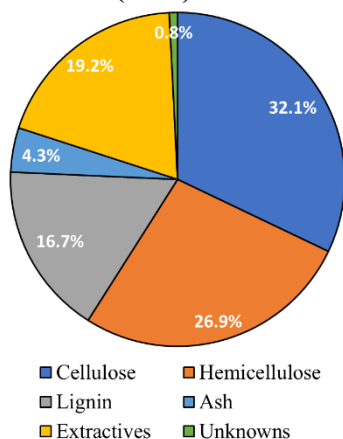
Appendix

Biochemical Analysis

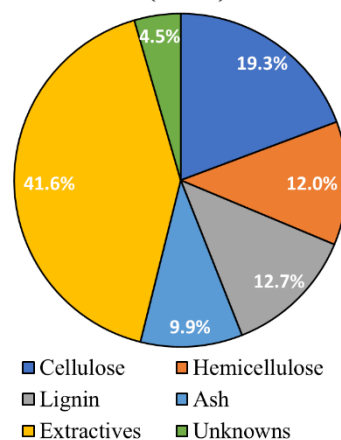
This section presents supplementary biochemical characterisation data collected during preliminary experiments. These results provide additional detail on feedstock composition and analysis, complementing the discussion in the main thesis.



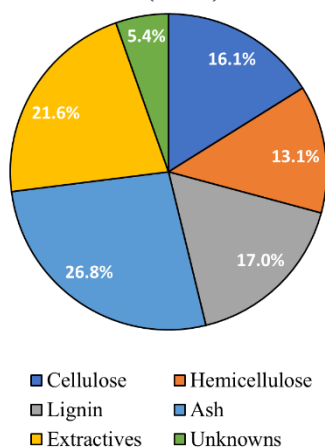
**Wheat Straw
Biochemical Composition
(wt.%)**



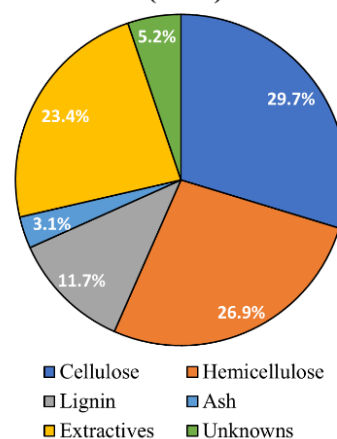
**Brussel Sprout Residue
Biochemical Composition
(wt.%)**



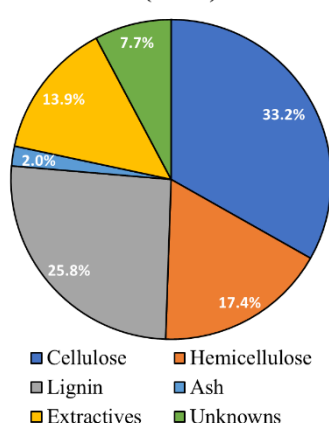
**Water Hyacinth
Biochemical Composition
(wt.%)**



**Corn Cob
Biochemical Composition
(wt.%)**



**Peanut Shells
Biochemical Composition
(wt.%)**



**Beechwood
Biochemical Analysis
(wt.%)**

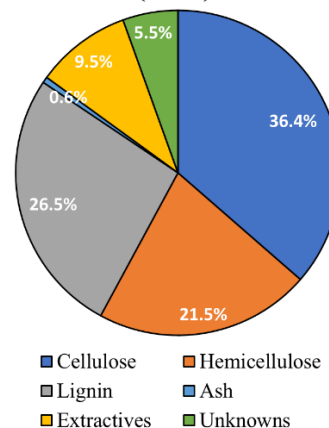


Figure A1. Supplementary biochemical analysis results obtained during preliminary experiments. These charts present feedstock composition and analytical reproducibility data that were not included in the main body of the thesis. Together, they provide additional context on the biochemical properties of the raw materials used in subsequent alcoholysis studies.

Ethanolysis

The following figures show additional ethanolysis data and analyses. These results were not included in the main body but are presented here to illustrate broader experimental trends and provide supporting information for the ethanolysis study.

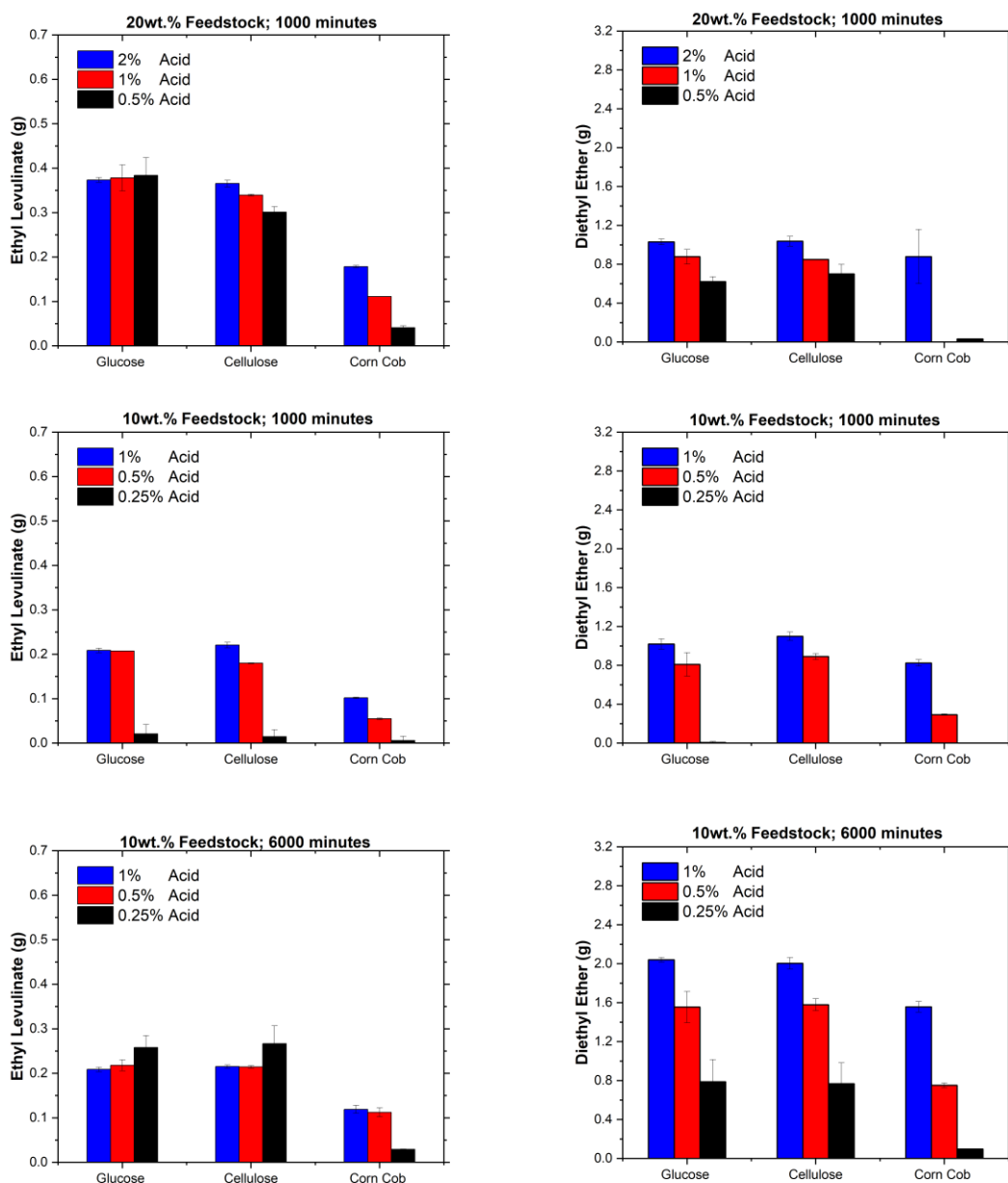


Figure A2. Supplementary ethanolysis results at 150 °C for three different feedstocks, showing product distributions at two time points: 1000 minutes (kinetic phase) and 6000 minutes (steady-state phase). Plots are presented for 10 wt.% and 20 wt.% feedstock loadings under varying acid catalyst concentrations. These data provide additional insight into the influence of feedstock type, catalyst loading, and feed concentration on reaction progression and final yields, complementing the results presented in the main text.

Multiple Linear Regression for Ethanolysis Literature

This section contains supplementary regression models and literature comparisons that support the ethanolysis analysis. The statistical treatment of literature data is included to illustrate the influence of reaction conditions on ethyl levulinate yield.

A detailed literature review was performed on the alcoholysis of glucose to produce ethyl levulinate in ethanol solvent, for various catalysts in a one-pot process. From the data gathered (30 reported yields of ethyl levulinate from glucose), multiple linear regression (MLR) was performed to identify which reaction conditions were statistically significant with regard the production of ethyl levulinate. The independent reaction variables used in the regression were:

- Feedstock concentration
- Ethanol concentration
- Catalyst concentration
- Catalyst type
- Reaction temperature
- Reaction time

From this analysis, no reaction conditions were determined to be statistically significant. The two most common categories of catalyst used were:

1. Inorganic mineral acid and metal salts.
2. Zeolite based catalysts.

A MLR model was separately created for each catalyst type. Within each catalyst type, models were produced for every combination of the independent variables (reaction conditions). The p-value of each coefficient for the reaction conditions were calculated for each model produced. The p-values are indicators that represent how statistically significant an independent variable is and are found using the probability of the observed data occurring by chance. It was found that for both zeolite based and Inorganic mineral acid and metal salt catalysts, both feedstock loading and reaction temperature were statistically significant variables on the yields of ethyl levulinate from glucose. However, there was not enough data to draw any meaningful conclusions. The models produced from MLR are shown in figures A3 and A4.

$$-0.47 * \text{Feedstock (mass\%)} + 0.21 * \text{Temperature(}^{\circ}\text{C)} = \text{Yield of Ethyl Levulinate (mol\%)}$$

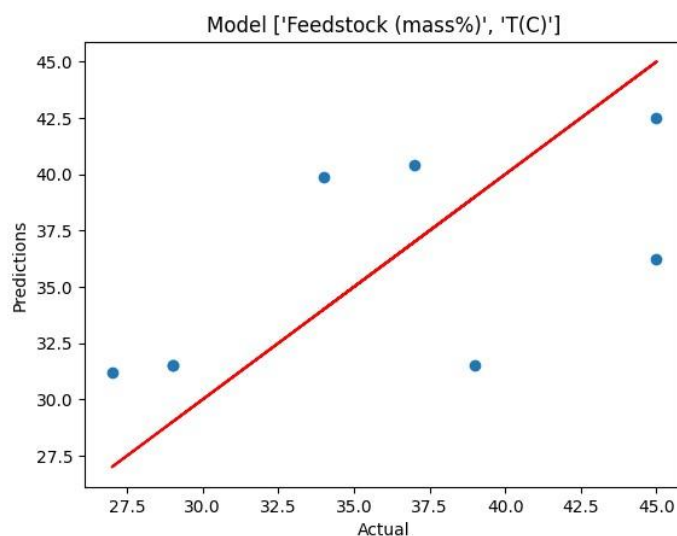


Figure A3. Predicted ethyl levulinate yields (mol%) versus the actual yields (mol%) reported from the literature based on two reaction conditions: feedstock loading (mass%) and reaction temperature ($^{\circ}\text{C}$). This model only considers glucose as a feedstock and Inorganic mineral acid and metal salts as catalysts. The model's equation is presented above the plot shown.

$$-3.80 * \text{Feedstock (mass\%)} + 0.29 * \text{Temperature(}^{\circ}\text{C)} = \text{Yield of Ethyl Levulinate (mol\%)}$$

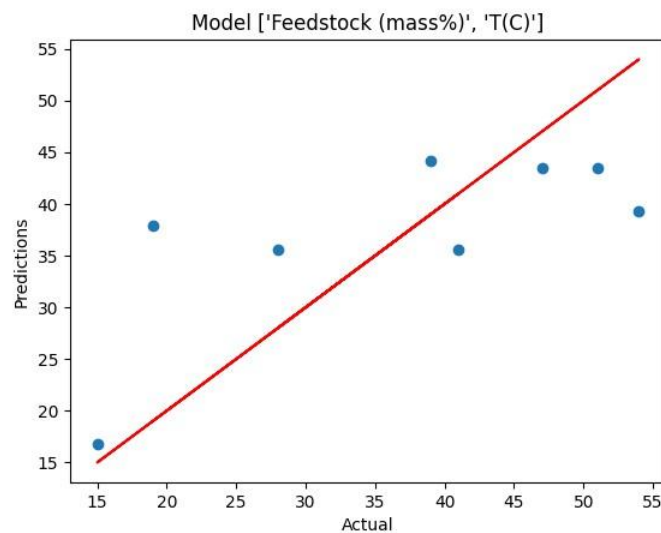


Figure A4. Predicted ethyl levulinate yields (mol%) versus the actual yields reported from the literature based on two reaction conditions: feedstock loading (mass%) and reaction temperature ($^{\circ}\text{C}$). This model only considers glucose as a feedstock and zeolite based materials as catalysts. The model's equation is presented above the plot shown.

Butanolysis

Supplementary graphs for the butanolysis of glucose, cellulose, xylan, and corn cob are presented in this section. These data expand on the results in the main text and provide further insight into how feedstock type influences alkyl levulinate yields.

Glucose

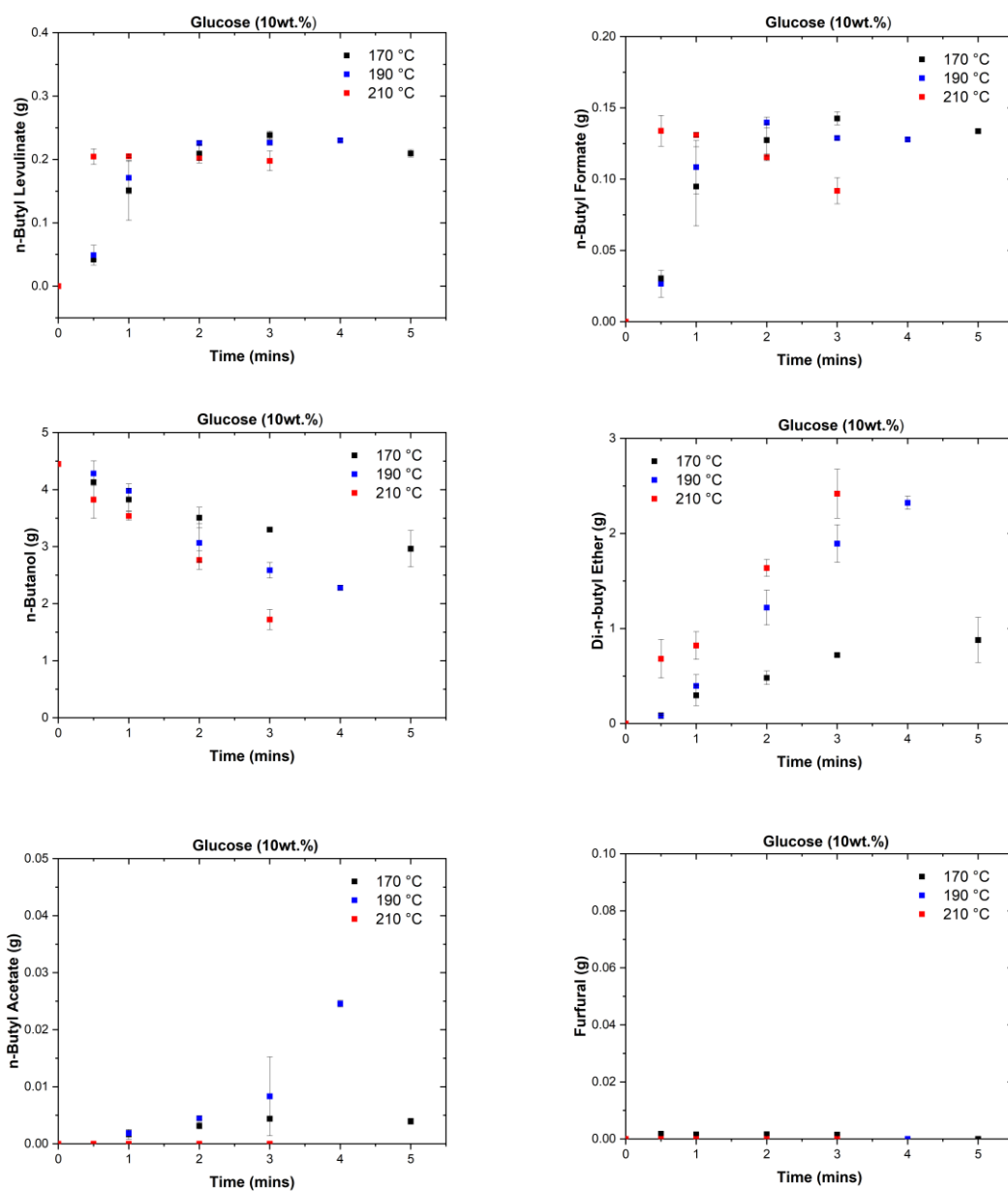


Figure A5. Supplementary butanolysis results for glucose at 10 wt.% feedstock loading with 1 wt.% H_2SO_4 catalyst. Product distributions are shown at three different reaction temperatures, illustrating the effect of thermal conditions on alkyl levulinate formation.

Cellulose

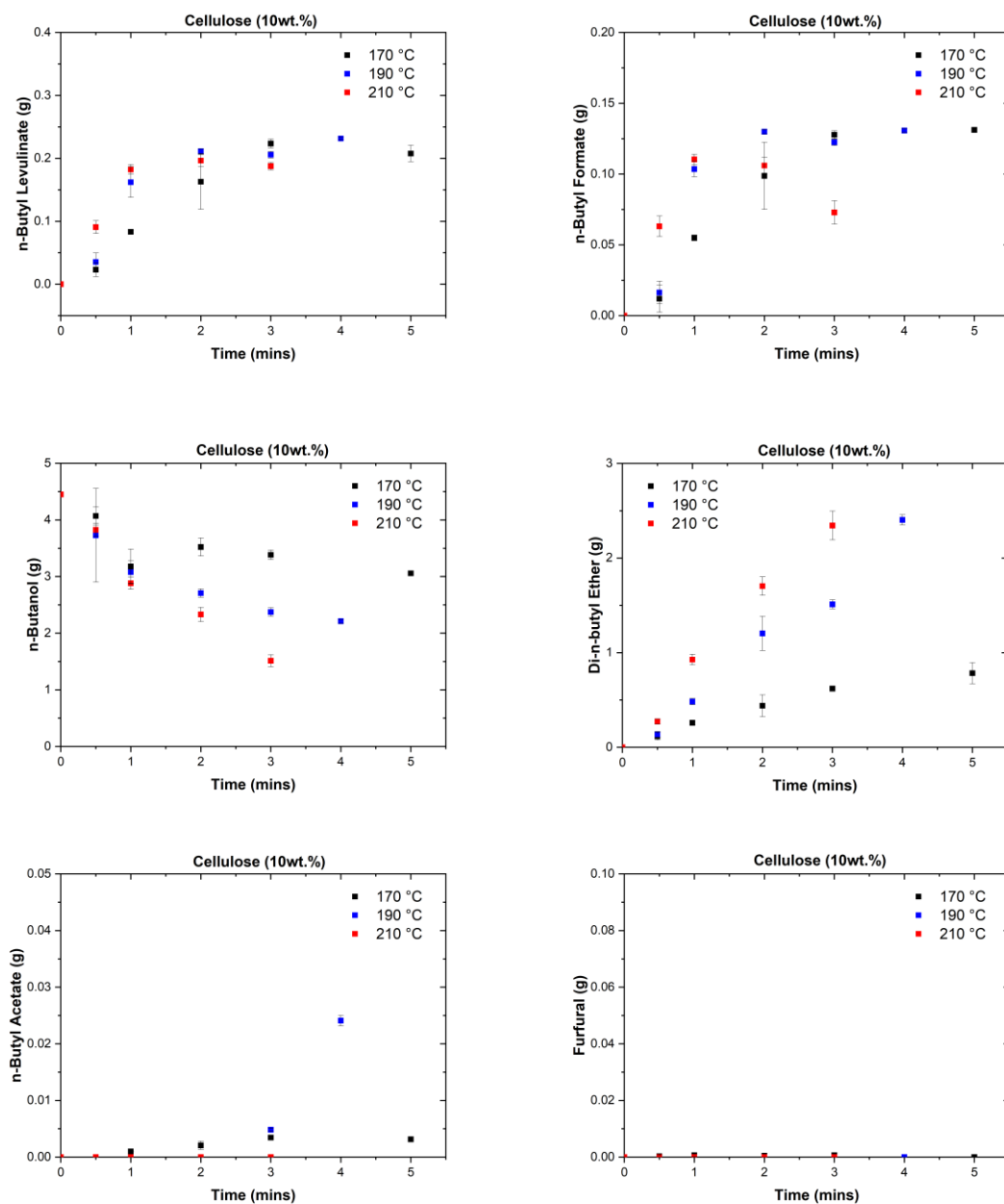


Figure A6. Supplementary butanolysis results for cellulose at 10 wt.% feedstock loading with 1 wt.% H₂SO₄ catalyst. Graphs display product distributions at three temperatures, highlighting the temperature dependence of conversion and yield trends.

Xylan

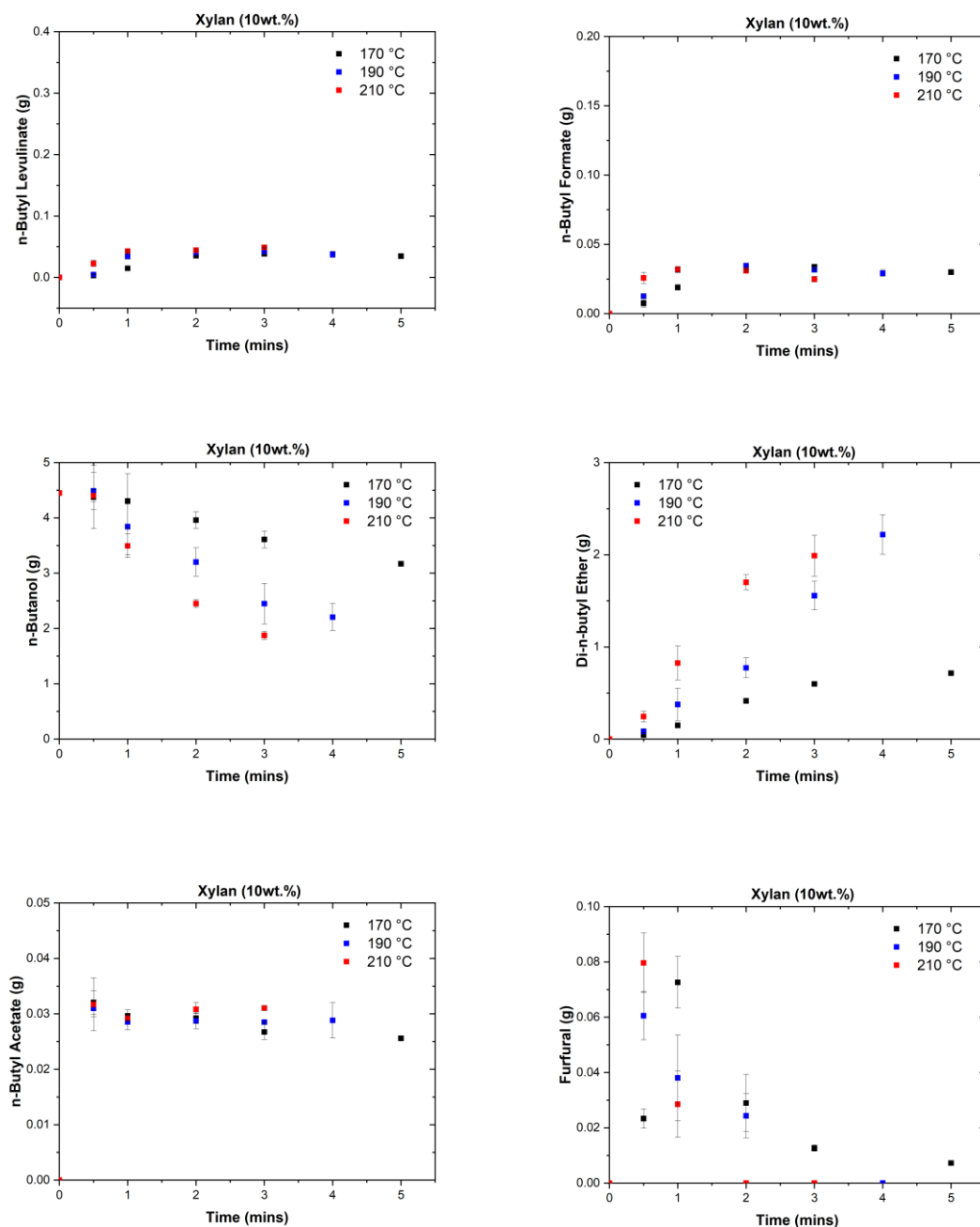


Figure A7. Supplementary butanolysis results for xylan at 10 wt.% feedstock loading with 1 wt.% H₂SO₄ catalyst. Data are presented for three different reaction temperatures, providing additional insight into feedstock-specific reactivity.

Corn Cob

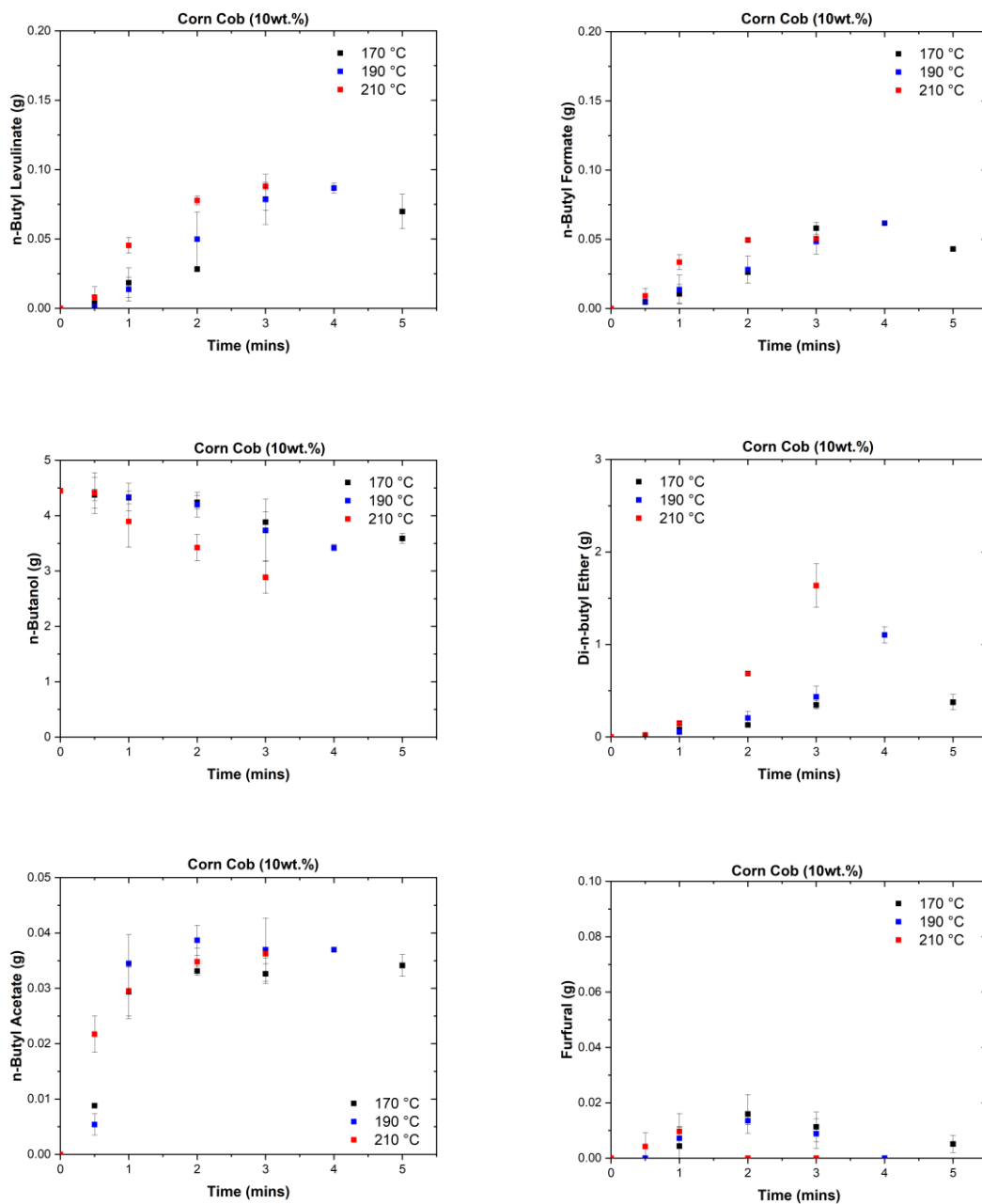


Figure A8. Supplementary butanolysis results for corn cob at 10 wt.% feedstock loading with 1 wt.% H₂SO₄ catalyst. Product distributions at three temperatures are shown, reflecting the variability of lignocellulosic feedstock behaviour under butanolysis conditions.