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Fusel Oil Valorisation via Solvent Extraction Distillation and Reactive Distillation: Experimental Characterisation and Process Simulation Using Aspen Plus and Aspen HYSYS

BY

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APPROVAL FORM

The undersigned certify that they have supervised, read and recommend to the Bindura University of Science Education for the acceptance of a research dissertation entitled: **Fusel Oil Valorisation via Solvent Extraction Distillation and Reactive Distillation: Experimental Characterisation and Process Simulation Using Aspen Plus and Aspen HYSYS**



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DECLARATION

I, Polite Mudyiwa, am officially declaring to the Bindura University of Science Education that this dissertation is a product of my original research, and borrowed ideas are cited accordingly as references. I also declare that the current work has not been presented to any educational institution for any educational merit purposes.

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ABSTRACT

Fusel oil (FO), a higher alcohol by-product of bioethanol fermentation, is routinely discarded as waste in distilleries across the developing world, despite its considerable potential as a source of value-added chemicals. This study investigates the valorisation of crude FO sourced from a Zimbabwean ethanol plant through experimental characterisation and Aspen process simulation. The FO was first dehydrated using gravity separation followed by anhydrous sodium sulphate drying, reducing the water content from 13.8% to 0.76% an overall removal efficiency of approximately 94.4%. GC-MS analysis confirmed isoamyl alcohol as the dominant component at 64.10 wt. % in the dried feed, alongside significant active amyl alcohol (14.04 wt. %) and ethanol (10.55 wt. %). Physical characterisation yielded a density of 0.832 g/mL and a kinematic viscosity of 3.87 mm^2/s, both consistent with higher alcohol rich FO literature values. Two valorisation pathways were then simulated. The first, a two-column solvent extraction distillation using n-hexane at a 0.3:1 mass ratio in Aspen Plus, achieved an isoamyl alcohol purity of approximately 96.4 wt.% with a recovery yield of 94.8%, operating without decanter vessels by leveraging upstream drying. The second, a reactive distillation esterification process simulated in Aspen HYSYS, achieved an isoamyl alcohol conversion of 97.96% and produced a combined C5 acetate ester product at 96.48 wt. % purity and 82.67% recovery, exceeding the 95 wt. % commercial-grade threshold for flavour and fragrance applications. Both routes demonstrated strong alignment with comparable published studies, validating the technical feasibility of transforming Zimbabwean FO from an industrial waste stream into commercially relevant chemical products within a circular economy framework.

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LIST OF ABBREVIATIONS

AFDIS – African Distillers

DWC - Dividing wall column

FO- Fusel oil

GC-MS- Gas chromatography–mass spectrometry

MoEPD- Ministry of Energy and Power Development

NRTL- Non-Random Two-Liquid

PFD- Process Flow Diagram

PTFE- Polytetrafluoroethylene

rtp- room temperature and pressure

1 CHAPTER 1: INTRODUCTION

1.1 Background

The increase in global energy demand has raised concerns about climate change and the depletion of fossil reserves, resulting in greater interest in the development of renewable and sustainable resources (Abrash Walton 2018). Biofuels from biomass have emerged as promising alternatives to fossil fuels due to their lower greenhouse gas emissions (Kaur et al. 2024). Among these biofuels, ethanol has gained significant attention and is used as a gasoline additive or substitute in many countries (Kunwer et al. 2022). Ethanol is also used as an industrial solvent, chemical feedstock, laboratory reagent, component of alcoholic beverages, preservative, antiseptic and pharmaceutical agent (Miklis et al. 2024).

Over the past twenty years, Zimbabwe's ethanol sector has undergone significant growth, largely propelled by national strategies aimed at reducing dependence on imported petroleum fuels and accelerating the transition toward renewable energy sources (Energy and Development 2019). Central to this development is the Chisumbanje Ethanol Plant, located in Manicaland Province, which employs sugarcane molasses as its principal feedstock for bioethanol production (Kambanje and Belete 2017). Consequently, thousands of litres of ethanol are distilled daily, producing substantial quantities of by-products, including vinasse, bagasse, and FO. Although vinasse and bagasse are effectively utilised in fertigation and cogeneration (Green Fuel 2025), FO remains largely overlooked, despite its rich chemical composition and significant potential for industrial valorisation.

FO is a mixture of C2 to C5 alcohols, consisting primarily of isoamyl alcohol alongside smaller fractions of ethanol, n-propanol and isobutanol (Patidar and Mahajani 2012; Tran et al. 2020). During fermentation, yeast produce higher alcohols either directly from sugars or indirectly from amino acids via the ehrlich pathway, with amino acids serving as the primary nitrogen source and being taken up slowly and sequentially from the wort or fruit must (Stanzer et al. 2023). The composition of FO varies depending on both the raw materials used in fermentation and how

efficiently it is separated from the fermented mixture (Mendoza-Pedroza et al. 2021; Sözen et al. 2016). Several factors can promote the formation of FO during ethanol production, including low nitrogen content in the fermentation medium, extended fermentation periods, and prolonged intervals between fermentation and distillation (Cardozo-filho 2023).

FO can be upgraded from a low-value fermentation by-product into valuable industrial products, such as isoamyl acetate, biodiesel components, bio-lubricants, fuel additives, and agrochemicals, through targeted separation and conversion processes. FO, which holds considerable potential as an alternative fuel for internal combustion engines(Neagu and Cursaru 2025), may act as a herbicide, causing damage to sugarcane plants when applied (Aparecida et al. 2017).

While distillation is a primary method for separating FO from ethanol due to differences in boiling points, several factors make it challenging to achieve a complete separation of its volatile components using simple distillation alone (Mendoza-Pedroza et al. 2021). FO is a complex mixture containing various higher alcohols like isoamyl alcohol, active amyl alcohol, n-propyl alcohol, and isobutyl alcohol, often with boiling points that are close to each other(Ferreira, Meirelles, and Batista 2013). This proximity in boiling points necessitates precise and often energy-intensive separation processes, and achieving high purity levels remains a challenge (Missyurin et al. 2024).

A significant complication is the presence of water in FO, which forms heterogeneous azeotropes with many of the higher alcohols(Ferreira et al. 2013). Azeotropes are mixtures that boil at a constant temperature and composition, meaning that simple distillation cannot separate them into their individual components(Missyurin et al. 2024). The formation of these azeotropes, particularly with water, means that a single distillation step may not yield pure alcohols and can complicate the separation process (Missyurin et al. 2024). Specialised techniques, such as fractional distillation with a high number of trays, dividing wall distillation columns, pressure-swing distillation, or hybrid approaches combining distillation with extraction, may be required for more effective separation (Ferreira et al. 2013). Phase equilibrium studies show that isoamyl

alcohol can be recovered from FO at high purity and low cost using a dividing wall column, which offers significant reductions in total annual cost compared to traditional distillation (Mendoza-Pedroza et al. 2021).

The growing demand for reusing waste from sugar and alcohol processes minimises the degradation of natural resources (Christine and Jaguaribe 2023). In this sense, it is of great importance in countries where there is a large production of ethanol to find alternatives for the use of waste generated in the process, making ethanol production less polluting and more profitable(Christine and Jaguaribe 2023).

In Zimbabwe, the specific utilisation and disposal pathways of FO within the bioethanol industry remain largely undisclosed and underexploited. Currently treated as a minor, secondary by-product, its role in the industrial value chain lacks transparency, often resulting in it being handled as a low-value waste stream despite its documented chemical potential. This lack of clear valorisation strategies represents a significant missed economic opportunity, as FO contains high-value higher alcohols which are essential for the production of flavours, fragrances, and pharmaceuticals(Cardozo-filho 2023). Furthermore, the absence of public data on its management poses potential environmental risks; without transparent, regulated processing, organic waste streams can inadvertently contribute to industrial pollution and resource inefficiency.

Transitioning from an opaque disposal model to a proactive valorisation model could transform Zimbabwe’s bio economy (Energy and Development 2019). By converting FO into value-added chemicals or renewable fuels, the sector can stimulate downstream industries and increase foreign exchange savings via import substitution(Makinia et al. 2014). Environmentally, repurposing FO aligns with circular economy principles to reduce the carbon footprint of ethanol production, while socially supporting rural development and strengthening the resilience of the Zimbabwean agro-industrial sector.

1.2 Problem statement

Despite the rapid expansion of Zimbabwe's bioethanol industry, FO remains a largely undocumented and underexploited by-product. While other derivatives like vinasse and bagasse have established industrial roles (Green Fuels, 2025), FO is frequently dismissed as a low-value secondary stream. This oversight persists despite its high concentration of valuable alcohols with proven applications in specialised fuels, solvents, fragrances, and pharmaceuticals (Cardozo-filho 2023). The transition toward sustainable valorisation in Zimbabwe is currently stalled by three critical gaps: a lack of detailed chemical characterisation of local streams, limited research into viable purification technologies, and the feasibility of producing isoamyl acetate via esterification, or using FO as a solvent, has not been demonstrated using locally sourced material. Consequently, significant opportunities for economic diversification, import substitution, and circular economy integration remain unrealised. Addressing these gaps through systematic characterisation and experimental evaluation of separation and valorisation strategies is essential to unlocking the full industrial potential of Zimbabwe's ethanol sector (Ministry of Energy and Power Development, Zimbabwe, 2019)(Energy and Development 2019).

1.3 Aim

To investigate the valorisation potential of FO produced in Zimbabwe through characterisation, purification, and evaluation of value-added applications such as esterification and solvent use.

1.4 Objectives

1. To characterise crude and dried FO from a Zimbabwean ethanol plant by determining its chemical composition (GC-MS), density, viscosity, and boiling range, in order to establish an experimentally grounded feed profile for process simulation.
2. To simulate a two-column solvent extraction distillation process in Aspen Plus using n-hexane as a co-solvent for the purification of isoamyl alcohol from dried FO.
3. To simulate a reactive distillation esterification process in Aspen HYSYS for the direct conversion of dried FO alcohols to acetate esters using acetic acid, and to assess the conversion, purity, and recovery of the resulting mixed C5 ester product.

4. To validate both simulation models against comparable published studies and benchmark the results against established literature, in order to assess the reliability of the simulation methodology and contextualise the performance of the proposed valorisation routes.

1.5 Justification and Significance of the Study

This research is timely and significant for several reasons. First, it aligns with Zimbabwe's national goals for sustainable industrial development and the adoption of a circular economy (NDS-2). Second, valorising FO can reduce environmental hazards associated with its disposal while creating new value chains in the biofuel, chemical, and agricultural sectors (Biofuels policy of Zimbabwe). Third, the study contributes to global discourse on bio-refinery optimisation by demonstrating how low-value by-products can be transformed into commercially viable resources (Missyurin et al. 2024). Fourth, the experimental findings will generate a foundational dataset to guide future industrial feasibility studies for ethanol producers in Zimbabwe (Kambanje and Belete 2017).

In conclusion, the significance of this study is that it proposes a shift in the local industrial perspective by transforming perceived waste into an economic asset, directly aligning with Zimbabwe's national goals for value addition and beneficiation. By demonstrating that FOs are a source of valuable secondary raw materials, this work opens new possibilities for the sustainable development of the domestic alcohol industry and the broader bio-economy (Podczarski et al. 2025).

1.6 Limitations

This study acknowledges several factors that may influence the interpretation and broader generalisation of the findings. Primarily, access to granular industrial data from ethanol production plants is often restricted by corporate confidentiality. Additionally, the chemical composition of FO is inherently variable; fluctuations in feedstock characteristics, fermentation conditions, and seasonal factors may impact the consistency of the characterisation results(Cardozo-filho 2022). Furthermore, because the simulation process configurations will not

be validated at pilot or industrial scale, and experimental verification through physical column will be necessary to confirm that the conversion, purity, and recovery values predicted by Aspen Plus and Aspen HYSYS can be reproduced under real operating conditions.

1.7 Delimitations

This study was intentionally scoped to ensure focus and practical relevance within the available resources. The investigation was restricted to FO sourced from a single Zimbabwean sugarcane-based bioethanol plant, as the primary intent was to evaluate valorisation potential within the local industrial context. Of the numerous separation technologies available, only two valorisation routes were examined; solvent extraction distillation and reactive distillation esterification selected on the basis of their established relevance in the literature and suitability for simulation within Aspen Plus and Aspen HYSYS. The study was further bounded to technical process performance only, with economic evaluation, capital cost estimation, and life cycle assessment excluded due to the unavailability of industrial-scale operational data. The esterification route was designed to produce a combined mixed C5 acetate ester product, as the negligible boiling point difference between isoamyl acetate and active amyl acetate rendered their complete separation technically unjustifiable. Finally, all simulation feed compositions were derived exclusively from GC-MS analysis of the locally sourced sample to ensure the modelling reflected actual Zimbabwean FO characteristics.

2 CHAPTER 2: LITERATURE REVIEW

2.1 Overview of bioethanol production

Bioethanol is a renewable fuel made from plant materials that provides a cleaner alternative to fossil fuels by reducing greenhouse gas emissions and supporting agriculture(Jain and Kumar 2024). Bioethanol production is more than a technical process; it is a strategic pillar of the global energy transition, where sustainability, economics, and innovation converge, and its success relies on feedstock selection, efficient fermentation, and integration into existing energy systems (Kaur et al. 2024). Bioethanol production is classified into four generations: First generation (1G) from food crops like corn and sugarcane, second generation (2G) from non-edible lignocellulosic residues, third generation (3G) from fast-growing algae, and fourth generation (4G) using engineered organisms that boost yields and capture CO_2 (Edeh and Edeh 2020).

First-generation bioethanol competes with food supplies, second-generation bioethanol faces high pre-treatment and enzyme costs, and all bioethanol is hygroscopic, meaning it absorbs water and can corrode fuel infrastructure (Edeh and Edeh 2020). To reduce costs in second-generation bioethanol, processes can be arranged as Separate Hydrolysis and Fermentation (SHF), where the two steps run in different vessels at optimal temperatures; Simultaneous Saccharification and Fermentation (SSF), where both occur in one reactor to avoid sugar inhibition; or Consolidated Bioprocessing (CBP), where a single engineered microorganism performs enzyme production, cellulose breakdown, and fermentation in one step (Edeh and Edeh 2020).

Bioethanol production involves pre-treatment to open up biomass, hydrolysis to release sugars, fermentation by microorganisms to produce ethanol, and distillation with dehydration to yield fuel-grade ethanol (Gupta and Gaur 2019; Moodley and Trois 2021; Siegmeier, Blumenstein, and Möller 2018). Distillation purifies the fermentation broth, separating ethanol (boiling point 78.3 °C) from water (100 °C) to raise its concentration from about 5–12% to fuel-grade purity of 99.5% (Bušić et al. 2018; Okuo, Otaraku, and Peter 2025). While distillation separates ethanol from the fermentation broth, FOs (higher alcohols) tend to concentrate in specific regions of the

distillation column(Cardozo-filho 2023). During fractional distillation, FOs accumulate in the rectifier section and are removed as a fraction containing ethanol and water, which can then be further distilled to recover ethanol separately from the FOs (Cardozo-filho 2023).

2.2 FO overview

FO, also known as the higher alcohol fraction, is a complex by-product formed during alcoholic fermentation (Awad et al. 2017). It takes its name from the German word Fusel for inferior spirits and is composed of higher alcohols with more than two carbon atoms, which are less volatile than ethanol (Cardozo-filho 2023; Sümer et al. 2023).

FO is a fermentation by-product rich in higher alcohols that can be transformed from a waste stream into valuable compounds through careful separation and purification (Cardozo-filho 2023). It is a mixture of alcohols such as isoamyl alcohol, ethanol, isobutanol, and propanol plus water, with its composition varying according to the raw material used in fermentation (e.g., sugarcane, barley, corn, rice, sugar beet) and the efficiency of separation from the fermented broth (Cardozo-filho 2023). The composition of FO also depends on fermentation conditions such as amino acids, assimilable nitrogen, temperature, aeration, and inoculum concentration, as well as the type of inoculum used (Mayer et al. 2015).

Its composition consists of an azeotropic mixture between C2-C5 alcohols (isoamyl alcohol, isobutanol, propanol, butanol and others) and water, in addition to small concentrations of aldehydes, fatty acids, esters and terpenes (Cardozo-filho 2023). I-amyl alcohol is the main constituent of FO. Besides i-amyl alcohol, short chain alcohols, water and high boiling point compounds are also found. Composition is affected by the origin of the samples, being richer in heavy compounds, those coming from sugar mills(Montoya, Gil, and Trujillo 2016). FO has an unpleasant odour and can be colourless, yellow, brown or green depending on the fermented substance, less dense than water, flammable, insoluble in water, and has a boiling temperature between (122 and 138) °C (Cardozo-filho 2022).

The formation of FO occurs through yeast metabolism of sugars, specifically via the Ehrlich pathway, where amino acids are catabolised to produce corresponding higher alcohols (Hazelwood et al. 2008). Extended fermentation or delays before distillation allow continued yeast metabolism that increases FO accumulation, whereas large fermenters with homogeneous conditions, optimised strains for high ethanol yield, and precise control of temperature, pH, and nutrients minimise FO generation (Kotarska, Dziemianowicz, and Świerczyńska 2025).

Global ethanol output continues to rise, with the United States and Brazil together accounting for 84% of production, the U.S. relying mainly on corn and Brazil on sugarcane (Timár, Báleš, and Volek 2021). Although FO yields are low compared to ethanol volumes, it accumulates in distilleries and poses disposal challenges, yet as a complex mixture it can supply technical alcohols for industries such as food, pharmaceuticals, organic synthesis, perfumes, cosmetics, paints, and varnishes; however, its use is complicated by difficult separation due to water forming low-boiling azeotropes with aliphatic alcohols (Missyurin et al. 2024). In ethanol manufacturing, residues such as FO, commonly called sugarcane oil, are generated during sugarcane processing, and while some mills sell it, most treat it as waste (Christine and Jaguaribe 2023).

Once considered a waste of alcoholic fermentation, FO has become a target for industrial recovery, and within a circular economy, it can serve as a raw material for value-added products while reducing environmental impact (Nogueira Marinho et al. 2025). FO, with its high isoamyl alcohol content (57.65–74) %, can act as an acyl acceptor in trans- and esterification reactions to produce flavouring esters, biolubricants, fuels, and fossil fuel additives; additionally, it shows herbicidal and fungicidal potential due to antimicrobial compounds such as octanoic acid, pyrazines, nerolidol, and farnesol (Cardozo-filho 2022). It contributes to the flavour and aroma of alcoholic beverages like whiskey and vodka and is used as a flavouring agent in perfumes and spirits (Cardozo-filho 2022). FO can serve as a clean, high-efficiency spark-ignition fuel with reduced nitrogen oxide (NOx) emissions, and its energy value is comparable to other alternative combustible fuels (Calam et al. 2015; Jain and Kumar 2024; Kunwer et al. 2022).

2.3 Separation and purification techniques of FO

Recovering individual higher alcohols from FO is technically challenging due to the close boiling points of its components and the formation of heterogeneous azeotropes, especially with water (Missyurin et al. 2024). Distillation efficiency was reported at 96.5% at the final boiling point (139.9 °C), ensuring separation of alcohol fractions without major loss of alcohol content (Sim, Saygın, and Özdalyan 2020). Parameters such as moisture content, acid value, density, and true boiling point (TBP) curves reveal how FO behaves during distillation and highlight impurities, water, fatty acids, and esters that complicate purification (Montoya et al. 2016).

Several methods exist for separating mixtures that form azeotropes; homoazeotropes can be separated either by pressure-swing distillation or by introducing separating agents (entrainers) (Cortel et al. 2024). Researchers addressing the challenge of FO separation have proposed a variety of solutions (Missyurin et al. 2024). For example, Marcela C. Ferreira et al. evaluated three options for separating FO to obtain isoamyl alcohol: a single-column process flow diagram (PFD) with a decanter side stream, a two-column PFD with a decanter on the first column distillate, and a configuration combining a decanter, stripper, and distillation column (Ferreira et al. 2013). José de Jesús Mendoza-Pedroza et al. propose the use of a dividing wall column (DWC) as an alternative to the conventional three-column configuration, considering a feed mixture of water, ethanol, and isoamyl alcohol with minor components, and applying total annual cost (TAC) as the efficiency criterion (Mendoza-Pedroza et al. 2021).

A method has been proposed for separating FOs using hexane as a low-boiling solvent in a batch distillation column, where the aqueous cut is removed first, followed by fractions of C2–C4 alcohols, isoamyl alcohol, a high-boiling cut, and finally the distillation residue (Missyurin et al. 2024). Techniques like azeotropic distillation, extractive distillation, and adsorption with molecular sieves are used to separate ethanol and water, indirectly improving FO purity (Cardozo-filho 2022). Better purification methods are essential to unlock FO’s potential in

producing esters, biodiesel, lubricants, and other value-added chemicals (Cardozo-filho 2023). Combining distillation, stripping, and decantation can yield nearly complete recovery of isoamyl alcohol with very high purity. This makes FO a promising option for recovering high-purity isoamyl alcohol, transforming a by-product into a valuable industrial raw material (Liz and Aleaga 2024; Sanchez and Trujillo 2011).

2.3.1 Conventional distillation

Since FO is a mixture of higher alcohols, distillation is required to separate and purify isoamyl alcohol (López-Fernández et al. 2022). The presence of azeotropes such as ethanol–water and ethanol–isoamyl alcohol complicates conventional distillation, while high water content further limits direct use of FO in fuels or chemical synthesis (Cardozo-filho 2022). A conventional distillation scheme typically employs three columns with decanters: Column I separates ethanol and water as distillate, Column II recovers azeotropic ethanol, and Column III (with a decanter) isolates isoamyl alcohol from the bottoms; while this achieves moderate purity, it is highly energy-intensive, with Column I alone accounting for about 83% of the thermal load 2021). The proximity of boiling points among isoamyl alcohol, active amyl alcohol, and isobutyl alcohol necessitates high-efficiency fractionation. Simple distillation columns with limited theoretical plates cannot achieve the required separation factors (Liz García Aleaga et al. 2025).

TBP curves divided FO into three zones: light alcohols (ethanol, propanol, and butanol), isoamyl alcohol, and heavy compounds (fatty acids, esters). This shows that fractional distillation can separate FO into useful fractions (Montoya et al. 2016). Fractional distillation using columns with a higher number of trays (typically exceeding 40-60 theoretical stages) enhances separation efficiency (Giwa et al. 2018); however the high energy demand and inability to cleanly resolve structural isomers such as iso amyl alcohol and active amyl alcohol represent fundamental limitations that necessitate more advanced separation strategies.

2.3.2 Extractive and azeotropic distillation

The presence of water-fusel alcohol azeotropes necessitates additional separation strategies. These methods employ separating agents such as hexane or acetic acid to break azeotropes, thereby improving separation efficiency (Liz García Aleaga et al. 2025). Extractive distillation introduces a high-boiling entrainer that selectively interacts with certain components, altering relative volatilities and thereby enabling the breaking of azeotropes (Speight 2020). Azeotropic distillation employs a third component (entrainer) that forms a new, lower-boiling azeotrope with one of the original mixture components, enabling its removal as distillate (Wu et al. 2024). While these methods effectively break azeotropes, the introduction of a third component adds complexity to solvent recovery and increases both capital and operating costs, which must be weighed against the purity gains achieved.

2.3.3 Adsorption with molecular sieves

Molecular sieves with 3Å pores selectively adsorb water from alcohol mixtures, enabling production of anhydrous ethanol and isoamyl alcohol without toxic entrainers (Baião Dias et al. 2018). A key advantage of molecular sieve adsorption is that it requires no solvent addition, which enables very high product purity and eliminates a solvent recovery step, and this process can be performed using a hydrophilic adsorbent with pore diameters sized to selectively adsorb water molecules while excluding ethanol and isoamyl alcohol molecules (Pinterich and Maciel 2023). Hybrid systems that pair simple distillation with molecular sieves achieve energy-efficient dehydration by avoiding the heavy steam demand of multi-stage azeotropic distillation (Patil 2016).

Despite these advantages, molecular sieve adsorption is most effective as a polishing step following upstream water removal rather than as a standalone purification method for complex multicomponent mixtures such as FO. The selective adsorption of water alone does not address the separation of higher alcohols from one another, meaning that molecular sieves must be integrated with distillation or extraction steps to achieve commercially relevant isoamyl alcohol purity. In the context of this study, upstream drying using anhydrous sodium sulphate served an

analogous function, reducing water content prior to distillation simulation thereby removing the need for molecular sieve integration in the proposed process configuration.

2.3.4 Solvent extraction

Non-polar solvents or hybrid decanter–distillation systems can selectively recover isoamyl alcohol, with solvent extraction reducing energy demand but requiring careful solvent recovery and environmental safeguards (Liz García Aleaga et al. 2025). The selective recovery of isoamyl alcohol is facilitated by the use of non-polar solvents, often integrated into a hybrid decanter–distillation system to achieve intensified separation (Missyurin et al. 2024). This solvent extraction approach offers a superior performance profile by significantly reducing energy demand relative to conventional distillation methods (Zhu et al. 2025). Despite its energy advantages, solvent extraction introduces concerns around solvent toxicity, recovery efficiency, and environmental compliance, factors that are particularly relevant in the Zimbabwean industrial context where solvent handling infrastructure may be limited.

2.3.5 Reactive distillation

Reactive distillation is a single piece of equipment that combines the work of a chemical reactor and a distillation column, letting both reaction and separation happen together (Baskar and Aiswarya 2016). Reactive distillation shows how reaction and separation can work hand-in-hand in one unit, with products removed as they form so the reaction goes further, giving higher conversions and saving energy (Rodriguez-Robles et al. 2019). Sometimes one reactant acts as an internal helper (entrainer), breaking at least one azeotrope, and since it has the highest boiling point and doesn’t form azeotropes with the others, it makes separation easier (Muñoz et al. 2023).

Reactive Distillation (RD) integrates chemical reactions with distillation, sometimes used to esterify FO components for easier separation (George S Brady, Henry R. Clauser 2002). It intensifies processes by integrating reaction and separation within a single unit (Mardani et al. 2016). Direct esterification of FO with acetic acid via reactive distillation (RD) eliminates the

preliminary alcohol separation step, achieving conversion rates up to 98.8% for isoamyl alcohol and producing isoamyl acetate at 98% purity while reducing energy consumption by about 30% compared to conventional distillation (Liz García Aleaga et al. 2025). Although reactive distillation offers significant process intensification benefits, its design complexity, particularly the need to simultaneously satisfy reaction kinetics and vapour-liquid equilibrium constraints within a single column presents considerable challenges for scale-up and control.

2.3.6 Dividing wall column

The Dividing Wall Column (DWC) is a process intensification innovation that integrates multiple separation stages into one unit, streamlining FO component recovery (Ye et al. 2022). Phase equilibrium studies show that isoamyl alcohol can be recovered from FO at high purity and low cost using a dividing wall column, which offers significant reductions in total annual cost compared to traditional distillation (Mendoza-Pedroza et al. 2021).

2.3.7 Hybrid and alternative separation technologies

Recent research has shifted from standalone distillation toward hybrid and alternative separation technologies to enhance FO recovery (Podczarski et al. 2025). Hybrid decanter–distillation process employs hexane as a separating agent, achieving near-complete water removal and highly pure isoamyl alcohol recovery, offering greater energy efficiency than conventional dividing wall column designs; however, solvent ratio optimization is critical, since excess hexane increases costs without improving separation (Missyurin et al. 2024).

Liquid–liquid extraction efficiently enriches isoamyl alcohol from aqueous FO mixtures by exploiting phase solubility differences, serving as a key pre-concentration step that reduces the thermal load on subsequent distillation (Mortimer and Fairweather 2026; Tamen and Vishnikin 2021). Recent studies have applied supercritical carbon dioxide extraction for FO fractionation, leveraging its tunable solvation properties to achieve solvent-free product recovery despite greater operational complexity (Cardozo-filho 2023). Pervaporation and nanofiltration facilitates

the molecular-weight-based separation of ethanol-water mixtures (Liang et al. 2026; Maniewska et al. 2026).

2.4 Global management practices and valorisation techniques of FO

Globally, FO management has shifted from disposal and low-value blending toward circular economy valorisation (Xu et al. 2026), where advanced biorefineries isolate and repurpose components into high-value esters, flavourings, solvents, and bio-based precursors under zero-waste protocols (Cardozo-filho 2023). Global distilleries are increasingly adopting FO valorisation strategies to align with zero-waste industrial targets (Yıldırım et al. 2026). Essential oils, aromas, and extracts from FOs play a key role in creating unique products that stand out in the market therefore the commercialization possibilities of natural chemicals is increasingly appreciated, and their market is growing (Podczarski et al. 2025).

2.4.1 Solvent production

FO is a valuable source for generating green solvents, particularly isoamyl acetate and refined isoamyl alcohol (Tran et al. 2020). Isoamyl alcohol, once refined from FO, can be used as an industrial solvent in paints and varnishes, a flotation agent, and a precursor for isoamyl acetate, a flavouring in perfumery and confectionery (Missyurin et al. 2024). Refining of isoamyl alcohol from FO was discussed in chapter 2.3 above and its esterification will be discussed in 2.4.2 below. Using FO as a feedstock for solvent production adds value to the biofuel industry by turning a by-product into high-value chemicals (Dias et al. 2020).

2.4.2 Esters production

Isoamyl alcohol, the primary constituent of FO can undergo esterification to produce isoamyl acetate an ester (López-Fernández et al. 2022). Esterification of isoamyl alcohol is typically done with acetic acid (or acetic anhydride) at temperatures around 80 °C, often using solid acid catalysts like sulphonated mesoporous silica for 3 hours, achieving up to 95% yield (Tran et al. 2020). Organic solvents, supercritical fluids, ionic liquids, and deep eutectic solvents are applied

to intensify enzymatic catalysis and enhance isoamyl acetate synthesis efficiency and yield (Guan et al. 2025).

The esterification process between acetic acid and isoamyl alcohol by a reactive distillation column results in 99.5% conversion of isoamyl alcohol with 88.4% w/w purity of isoamyl acetate (Aleaga et al. 2024). Liz García Aleaga et al proposes two approaches to produce isoamyl acetate from fuel oil; Isoamyl alcohol is first separated from FO by distillation and then esterified with acetic acid in a reactive distillation column, yielding isoamyl acetate with 99.05% purity at approximately 19.6 kg/h productivity and the other one the entire FO mixture reacts directly with acetic acid in a reactive distillation column, followed by purification in a second distillation column, producing isoamyl acetate with 98.10% purity at approximately 22.3 kg/h productivity while consuming about 30% less energy for heating and cooling (Liz García Aleaga et al. 2025).

2.4.3 Agro-industrial applications

FO applied both alone and in synergy with conventional herbicides, represents a promising path for sustainable weed management, and it only needs to 9be further explored scientifically to adjust doses and expand application technology (Aparecida et al. 2017; Pizzo et al. 2010). It is utilized as a penetrant that facilitates the absorption of other active ingredients (like glyphosate) into plant tissues (Pizzo et al. 2010). Mixing FO with glyphosate can lead to a 50% reduction in the required glyphosate dosage while maintaining over 92% weed control efficiency (Cardozo-filho 2022). FO acts primarily as a contact desiccant destroying plant surface tissues within 24 hours of application (Aparecida De Padua et al. n.d.). Mixing FO with glyphosate can reduce the dosage amount while maintaining maximum control over weed communities like Amaranthus. (Aparecida et al. 2017). Compounds like octanoic acid, farnesol, and nerolidol in FO contribute to its insecticidal, acaricidal, and fungicidal potential (Cardozo-filho 2022)

2.4.4 Renewable biofuel and fuel additive

FO can be used as an alternative fuel in internal combustion engines due to the amount of alcohol it contains (Sim et al. 2020). FO is positioned as a candidate for renewable energy, with

patents and research on catalytic processes and engine performance (Nogueira Marinho et al. 2025). Its lower heating value (LHV) is roughly 25% lower than gasoline, but its superior anti-knock properties and oxygen content make it an effective additive for modern, high-compression engines (Safieddin Ardebili et al. 2020; Sim et al. 2020). Blending with gasoline/ethanol, combustion performance, and environmental implications, highlights FO's potential to improve octane rating and energy density, while also noting challenges in purification and engine compatibility (Sim et al. 2020). Gasoline blends containing FO, typically at 10–30% v/v, have been shown to perform best at around 30% (F30), where optimized high-compression engines achieve up to a 17.2% improvement in brake thermal efficiency (Sim et al. 2020; Simsek and Ozdalyan 2018).

2.4.5 Summary of literature and research gaps

The literature collectively demonstrates that FO is a chemically complex, high-value by-product whose full industrial potential remains unrealised, particularly in developing-world distillery contexts. Numerous separation technologies have been evaluated globally, with solvent extraction distillation and reactive distillation emerging as the most technically promising routes for isoamyl alcohol purification and acetate ester production respectively. Critically, the performance of any proposed valorisation process is highly sensitive to feed composition, water content, and thermodynamic model selection factors that are feedstock-specific and cannot be reliably extrapolated from foreign industrial contexts to Zimbabwean material. This underscores the necessity of the experimental characterisation and locally grounded simulation approach adopted in the present study.

3 CHAPTER 3: METHODOLOGY

3.1 Research design

In this study, experimental analysis was combined with process simulation to valorise crude FO obtained from a Zimbabwean ethanol plant. The oil was first characterised in the laboratory to determine its chemical composition, density, boiling range and viscosity using GC-MS analysis and standard physical property measurements. These experimental data were then used as inputs for process simulations in Aspen. Using the simulation, two approaches were examined for separating the components of FO: solvent extraction distillation and reactive distillation (esterification) to produce i-amyl acetate. To ensure reliability, the simulation results were compared with published literature data.

3.2 FO drying

Free and dissolved water was removed by gravity separation and chemical separation respectively.

3.2.1 Gravity separation of aqueous phase (removal of free water)

Gravity separation works by exploiting differences in density between particles or liquid phases, allowing heavier components to separate from lighter ones under the influence of gravity (Tao, Youcai, and Nyankson 2023).

Purchased FO was transferred into a clean, dry 500 ml separatory funnel, with the stopcock closed. The mixture was allowed to stand for 24 hours to separate the aqueous phase by gravity. Subsequently, the lower aqueous layer was discarded and the organic layer was retained (Neagu et al. 2025).

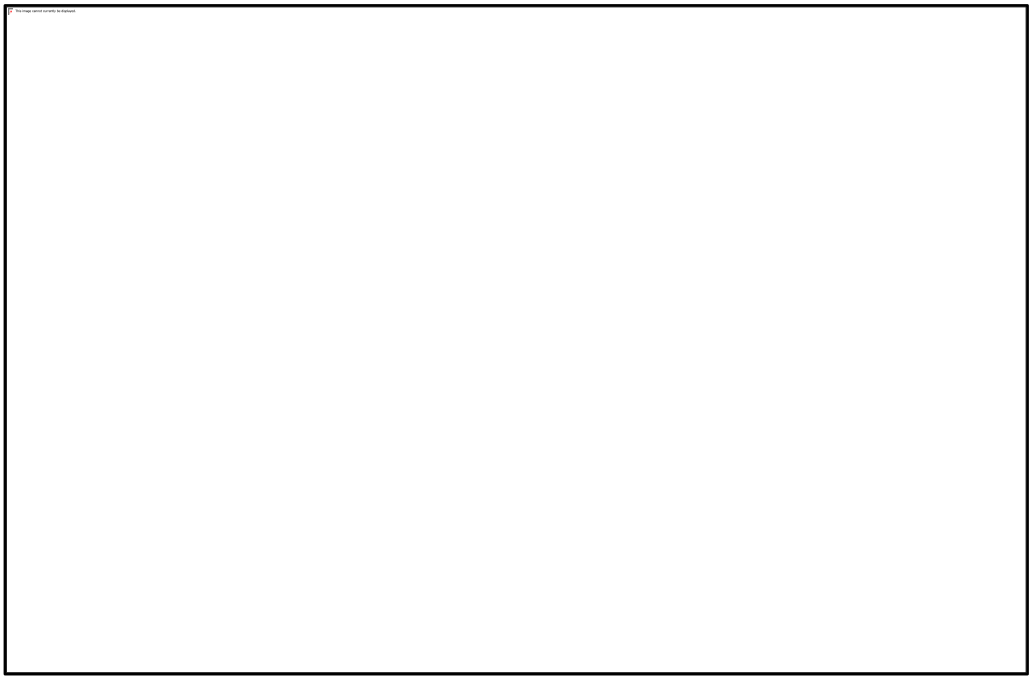


Figure 3.1 Separation of the aqueous phase

3.2.2 Chemical drying (removal of dissolved water)

Anhydrous sodium sulphate (Na_2SO_4; AR grade, ≥ 99.5% purity; Fisher Scientific, UK) was used to remove residual moisture from the product stream.

Chemical drying was done using the procedure from (Elchemy 2025).

The retained FO was dried by adding anhydrous sodium sulphate (Lisa Nichols 2023). Approximately 10g was added per 100 ml of FO, gently swirled and allowed to stand for 30 minutes to ensure complete water absorption. Upon addition, the drying agent initially formed clumps as it absorbed water from the sample. The mixture was left to stand for about 30 minutes, with occasional gentle swirling to enhance contact between the sodium sulphate and the liquid. Drying was considered complete when the sodium sulphate remained as free-flowing granules at the bottom of the container and the FO appeared clear and free of visible water.

The dried sample was filtered through Whatman number 1 filter paper into a clean, dry Schott bottle. The bottle was sealed with PTFE-lined cap and stored at rtp in a dark cupboard to avoid

photo degradation. This dried FO was served as the feed material for all subsequent characterisation.

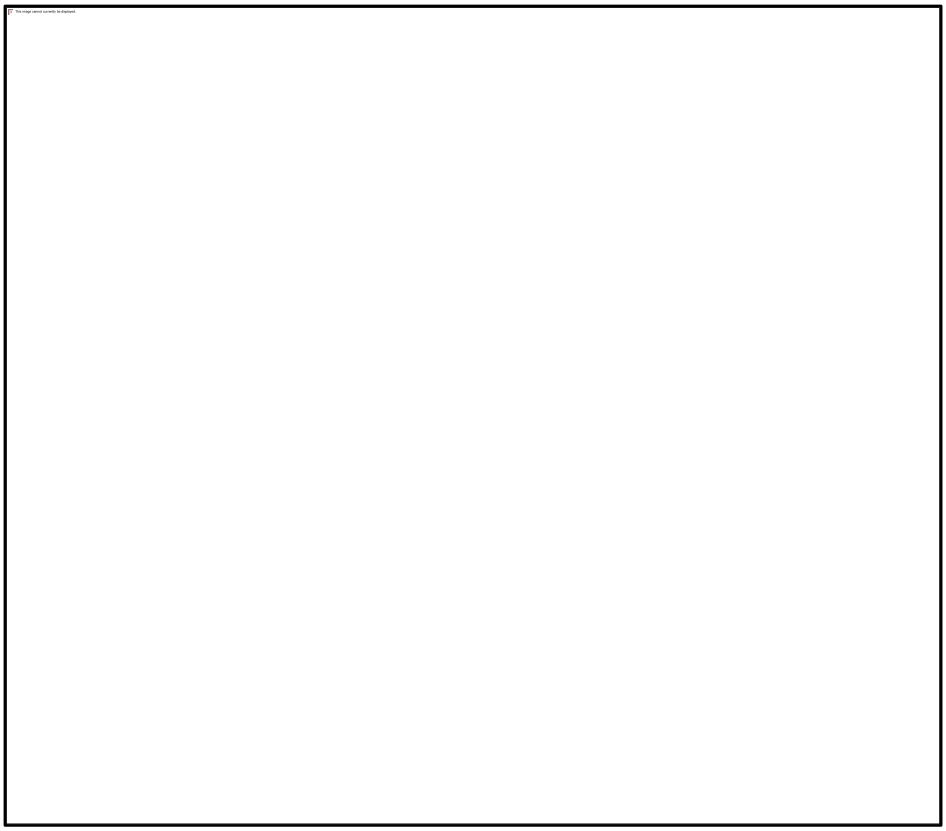


Figure 3.2 FO chemical drying

3.3 Characterisation of FO

When choosing a strategy for processing a given waste, its chemical composition, qualities, and the process in which it was formed should be taken into account (Studziński, Gackowska, and Dadzibóg 2023); therefore, in this study FO was characterized before separation and valorisation simulations. Density, viscosity and boiling range were determined for dried FO whilst GC-MS was done for both crude and dried FO.

3.3.1 GC–MS Analysis of FO

GC–MS is a powerful analytical technique that combines gas chromatography and mass spectrometry to separate, identify, and characterise the chemical compounds present in a sample (Sparkman, Penton, and Kitson 2011). By combining efficient separation with precise molecular identification, GC–MS provides a highly reliable method for analysing complex chemical mixtures. Gas chromatography is used to determine the proportion of isoamyl alcohol and to identify water composition and other alcohols present in FO (López-Fernández et al. 2022).

The FO sample was diluted with hexane to obtain a suitable concentration for injection. A volume of 2 µl of the prepared solution was introduced into the GC–MS instrument. The chromatogram was recorded under the operating conditions specified for the column and carrier gas. The mass spectra corresponding to the chromatographic peaks were obtained simultaneously. Peak identification was carried out by comparison with authentic standards and by matching the acquired spectra against reference libraries. The percentage composition of the FO sample was determined from the relative peak areas of the identified compounds. This procedure was done for crude and for dried FO.

The GC-MS model was **Agilent 6890 GC with 5973 Mass Selective Detector (MSD)** with parameter settings below

Table 3.1 GC-MS parameter settings

Parameter	Setting
Column	HP-5MS (30 m × 0.25 mm × 0.25 µm)
Carrier gas	Helium (1.0 mL/min)
Injector temp.	250 °C
Oven program	40 °C (2 min) → 10 °C/min → 250 °C (5 min)
Ionisation	EI (70 eV)
Mass range	35–400 m/z

3.3.2 Density determination

This method was adopted from (Chukwuma Obinna Stanely 2022). The density of FO was determined using 25 ml pycnometer at 20 ± 0.5 ℃. The pycnometer and its stopper were first thoroughly washed and dried in an oven to remove any residual moisture that could affect the measurements (Bilal et al. 2020). The clean, dry pycnometer with its stopper was first weighed, and the mass was recorded as W1. The pycnometer was then filled with dried FO until slight overflow occurred through the capillary side tube, ensuring that no air bubbles were trapped inside, the stopper was inserted, and excess oil wiped from the outside and weighed again, giving a mass of W2 (Karem and Taha 2024). To improve the reliability and precision of the results, the entire procedure was repeated three times, and the average value was used in subsequent calculations. The density of the FO was calculated using the following relation:

$$density = \frac{W2 - W1}{volume\ of\ the\ bottle(25\ ml)}$$

3.3.3 Viscosity determination

The viscometer was cleaned with acetone and dried, mounted vertically in the constant temperature bath and allowed to reach thermal equilibrium then filled with FO, this was done because alcohols changes viscosity with change in temperature (Zhang et al. 2019) . The sample was allowed to flow by gravity and the flow time between the calibration marks was recorded. The measurement was repeated three times and average flow time was calculated. From (Peter Atkins 2010), The viscosity of the FO was then calculated using the standard relations applicable to the viscometer employed.

$$\acute{\eta} = \mathrm{Kt}$$

where:

ή = Kinematic viscosity of the sample (mm^2/s)

K = viscometer constant (supplied by the manufacturer, determined by calibration with a liquid of known viscosity (mm^2/s^2))

t = measured flow time (s)

A viscometer constant (K) of 0.01 mm^2/s^2 was used

3.3.4 Boiling range determination

The boiling range of the FO sample was determined using a simple distillation setup. Approximately 50 mL of the sample was placed in a round-bottom flask and heated gradually using a heating mantle. A thermometer was positioned at the distillation head to accurately record vapour temperature. The temperature at which the first drop of distillate appeared was recorded as the initial boiling point, while subsequent temperatures were recorded throughout the distillation process. The final temperature at which distillation ceased was also noted. The boiling range was then reported as the temperature interval between the initial and final boiling points.

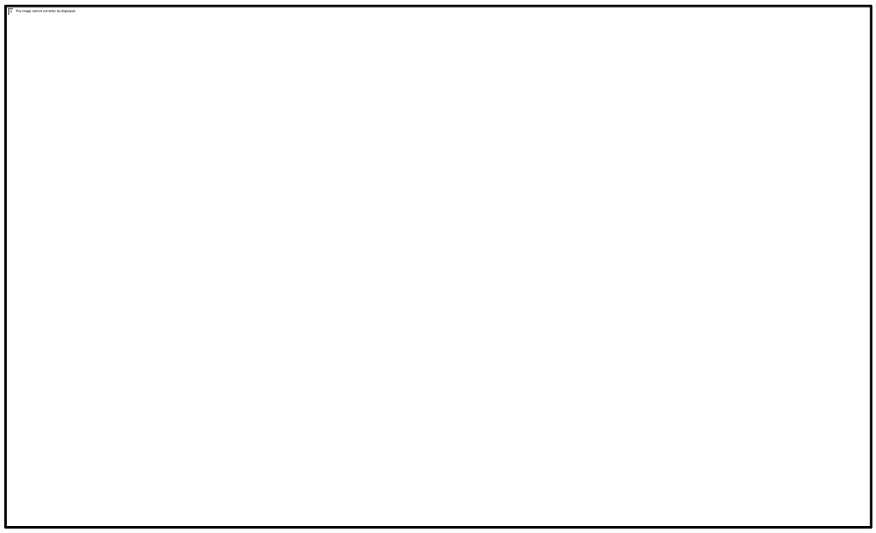


Figure 3.3 Boiling range determination

Colour changes to brick red due to presence of some carbonyls and impurities.

3.4 Solvent extraction distillation (purification of isoamyl alcohol)

3.4.1 Introduction

The composition of dried FO from (section 3.3) was entered into aspen as the feed stream. If any components were not available in the aspen component database, they were estimated using the UNIFAC group contribution method. A non-polar solvent distillation process column (RadFrac model in Aspen Plus) was simulated to separate isoamyl alcohol from the FO mixture.

3.4.2 Process rationale

The dried FO contains trace water (0.76%), sufficient to form azeotropes with isoamyl alcohol. Following (Neagu and Cursaru 2025), n-hexane was added as a co-solvent to form a low boiling hexane-water-ethanol azeotrope. This allows water to be removed in the overhead of the first distillation column without needing a separate decanter. Two columns in series then produce purified isoamyl alcohol stream.

3.4.3 Component selection and feed composition

To model the separation of the dried FO mixture accurately, all relevant chemical components were first selected from the Aspen Plus component databank. The composition of the feed stream was then defined using the mass fractions obtained from GC-MS analysis, as shown below.

Table 3.2 Feed mass fractions

Component	Chemical Name	Mass Fraction
Ethanol	Ethanol	0.1055
1-Propanol	1-Propanol	0.0180
Water	Water	0.0076
Isobutanol	2-Methyl-1-propanol	0.0815
1-Butanol	1-Butanol	0.0060
Active Amyl Alcohol	2-Methyl-1-butanol	0.1404
Isoamyl Alcohol	3-Methyl-1-butanol	0.6410
Total		1.0000

Since FO is a complex mixture containing polar alcohols and small amounts of water, significant non-ideal behaviour is expected due to strong intermolecular interactions and the potential formation of azeotropes. To account for these effects and provide reliable vapour-liquid equilibrium (VLE) predictions, the Non-Random Two-Liquid (NRTL) property method was selected. This model is widely used for alcohol–water systems and offers good accuracy when simulating highly non-ideal liquid mixtures. The feed stream entered the simulation at 1000 kg/h FO flow rate and 300 kg/h hexane flow rate, a temperature of 25 °C and 1.2 bar pressure.

3.4.4 Primary Distillation Column (C1)

The FO feed was introduced into a RadFrac distillation column (C1) designed for the initial separation of light and heavy alcohol fractions.

- Number of theoretical stages: 20

- Feed tray 12 FO
- Feed tray 8 hexane
- Top pressure 1.1 bar
- Bottom pressure 1.2 bar
- Reflux ratio (molar) 1.0
- Total condenser and kettle reboiler configuration
- Ethanol and other light alcohols recovered in the overhead stream
- Bottom product enriched in C4–C6 alcohols, including isoamyl alcohol, active amyl alcohol, and hexanol

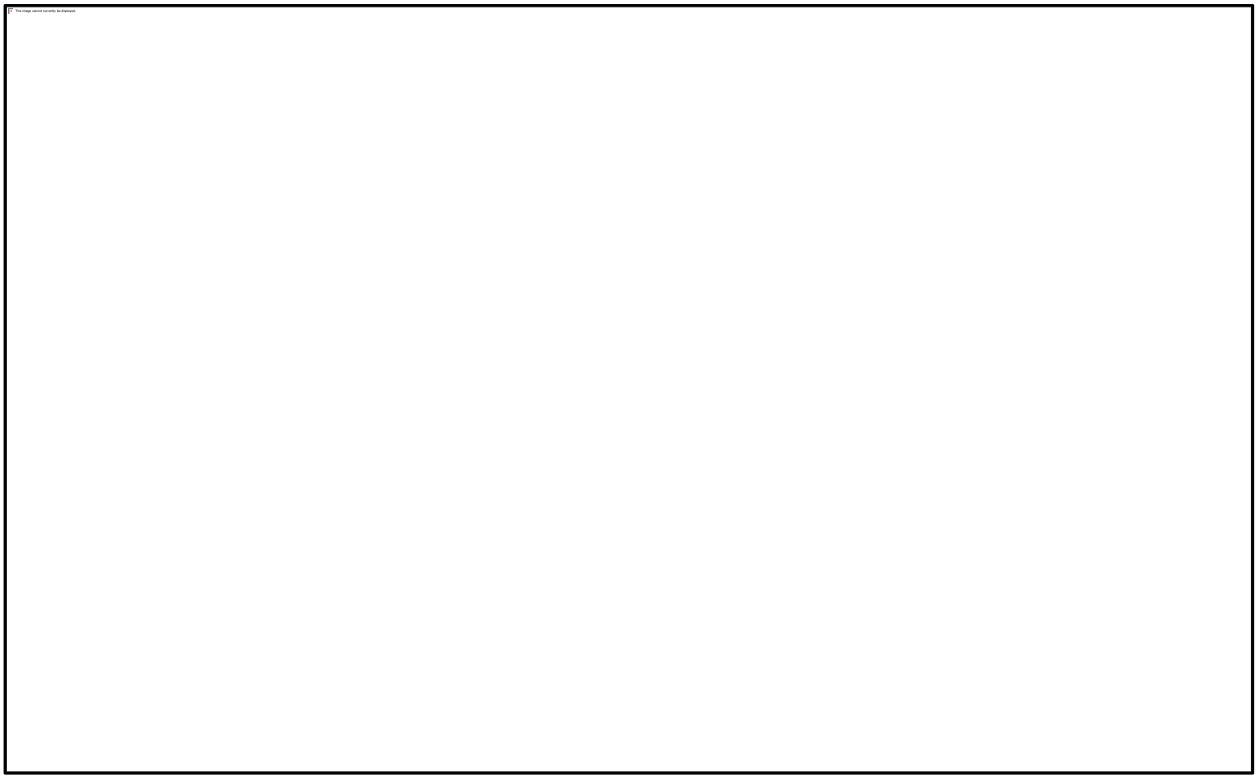
3.4.5 Secondary Distillation Column (C2)

- The bottom stream from C1 was fed to a second RadFrac distillation column (C2) bottom on stage 12, pressure 1.1 bar top, 1.2 bar bottom, reflux ratio 3.0 for further purification of the heavier alcohol fraction.
- Number of theoretical stages: 25
- Total condenser
- Kettle reboiler
- Isoamyl alcohol recovered in the bottoms stream
- Active amyl alcohol and hexanol remained as minor constituents

3.4.6 Convergence Criteria

The process simulation was solved using the standard Aspen Plus convergence algorithms. Convergence was considered successful when all material and energy balances were satisfied and the specified numerical tolerance criteria were achieved. A composition tolerance of less than 10^{-4} was used to ensure the accuracy and stability of the simulation results.

Figure 3.4 Isoamyl alcohol purification simulation



3.5 Simulation of reactive distillation (esterification)

3.5.1 Process rationale

In this direct processing approach, the alcohols present in the dried FO feed including isoamyl alcohol, active amyl alcohol, isobutyl alcohol, n-propanol, and ethanol are reacted simultaneously with acetic acid in a single batch reactor. Rather than isolating individual alcohol components before reaction, the entire FO stream is converted directly into value-added esters. This strategy maximizes feedstock utilization and is consistent with the integrated valorization approach reported by (Liz García Aleaga et al. 2025).

The process configuration was adapted from the direct esterification technology proposed by García Aleaga et al. (2025), which demonstrated the technical feasibility of converting FO alcohols into acetate esters through integrated reaction and separation. The main difference in the present study was the use of the dried FO composition obtained from the preceding dehydration section.

Following esterification, the reaction products were purified through conventional distillation to recover a mixed C5 ester stream composed primarily of isoamyl acetate and active amyl acetate. Due to the small difference in boiling points between these compounds, complete separation was not considered economically justified and the esters were therefore recovered as a combined product. Consequently, the process is designed to produce a mixed C5 ester product, which retains considerable commercial value for applications in the flavour, fragrance, and solvent industries

3.5.2 Thermodynamic model

The simulation was performed using Aspen HYSYS V14. The NRTL property package was selected for the liquid phase because of the highly non-ideal behaviour of alcohol–water mixtures. The combined NRTL–PR property method was adopted to represent vapour–liquid equilibrium throughout the process.

3.5.3 Process simulation, reaction stoichiometry and conditions

The dried FO stream from Section 3.5 was fed to the esterification system together with acetic acid. The acetic acid feed rate was specified using a Set operation to maintain a molar ratio of 1:1 relative to the total alcohol content of the FO stream, consistent with the conditions reported by García Aleaga et al. (2025). The reactions were represented as equilibrium reactions within the HYSYS column environment. All major alcohols in the dried FO feed undergo acid catalysed esterification with acetic acid as shown below:

Table 3.3 Esterification reactions for FO

Alcohol	Reaction	Product
Isoamyl alcohol (3-methyl-1-butanol)	$C_5H_{11}OH + CH_3COOH \rightleftharpoons CH_3COOC_5H_{11} + H_2O$	Isoamyl acetate
Active amyl alcohol (2-methyl-1-butanol)	$C_5H_{11}OH + CH_3COOH \rightleftharpoons CH_3COOC_5H_{11} + H_2O$	Active amyl acetate
Isobutyl alcohol	$C_4H_9OH + CH_3COOH \rightleftharpoons CH_3COOC_4H_9 + H_2O$	Isobutyl acetate
n-Propanol	$C_3H_7OH + CH_3COOH \rightleftharpoons CH_3COOC_3H_7 + H_2O$	Propyl acetate
Ethanol	$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$	Ethyl acetate

The operating conditions adopted from García Aleaga et al. (2025) are summarized below:

Table 3.4 Esterification reaction condition

Parameter	Value
Column type	Reactive distillation column
Acetic acid : total alcohol molar ratio	1 : 1
Feed temperature	90 °C
Pressure	1 atm
Reaction zone	Stages 5-20
Reflux ratio	1

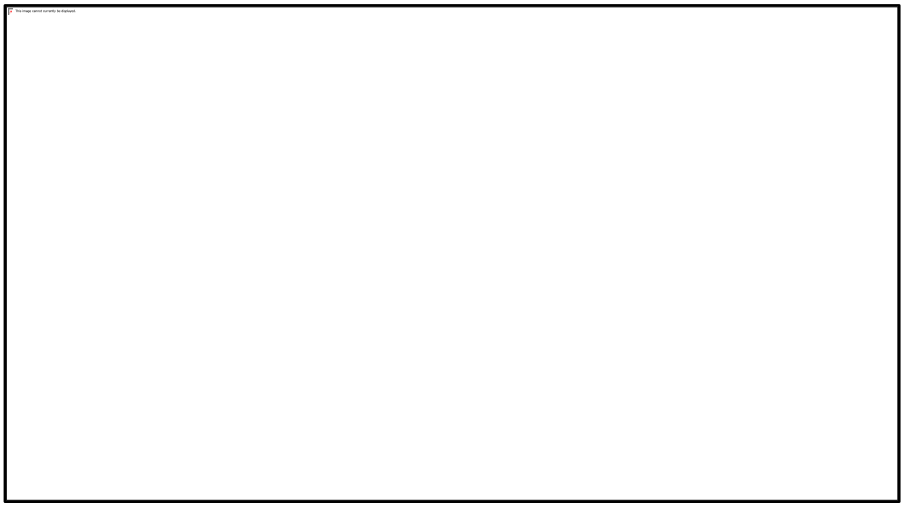


Figure 3.5 Reactive distillation PFD

3.5.4 Definition of process streams equipment

Table 3.5 Definition of process streams equipment

Symbol	Definition	Purpose
FO	Dried FO feed stream from the dehydration section.	Supplies the alcohols required for esterification.
IC-1	Feed-effluent heat exchanger (interchanger).	Recovers heat from the hot ester-rich stream and preheats the incoming FO feed, reducing utility consumption.
Hot FO	Preheated FO stream leaving IC-1.	Provides a heated feed to the reactive distillation column, improving reaction and separation efficiency.
Acetic Acid	Fresh acetic acid feed stream.	Supplies the acid reactant required for esterification.
SET-1	Aspen HYSYS Set operation.	Automatically adjusts the acetic acid flow rate to maintain the specified acetic acid-to-alcohol molar ratio.

A Ac	Controlled acetic acid stream entering the reactive distillation column.	Delivers the required quantity of acetic acid to the esterification process.
RD	Reactive distillation column.	Simultaneously performs esterification and separation of reaction products.
Qc	Condenser duty of the reactive distillation column.	Removes heat from the overhead vapour to maintain column operation and condensation.
Qr	Reboiler duty of the reactive distillation column.	Supplies heat required for vapour generation, reaction enhancement, and separation.
D1	Distillate stream from the reactive distillation column.	Removes water, light alcohols, light esters, and other volatile compounds from the system.
B1	Bottoms stream from the reactive distillation column.	Transfers the ester-rich fraction to the heat recovery section.
B1′	Cooled ester-rich stream leaving IC-1.	Feeds the purification column after heat recovery.
P1	Purification distillation column.	Removes residual impurities and concentrates the desired C5 acetate esters.
Q_c	Condenser duty of the purification column.	Removes heat from the overhead vapour to facilitate separation.

3.5.5 Overall Process Description

The direct esterification process converts the alcohols present in the dried FO stream into their corresponding acetate esters through reaction with acetic acid in a reactive distillation column (RD). The alcohols considered in the simulation include ethanol, n-propanol, isobutanol, active amyl alcohol, and isoamyl alcohol.

Prior to esterification, the FO feed is preheated in a feed-effluent heat exchanger (IC-1) using thermal energy recovered from the reactive distillation bottoms stream. Acetic acid is introduced at a controlled molar ratio using an Aspen HYSYS Set operation (SET-1), which automatically adjusts the acid flow rate according to the alcohol content of the feed.

Within the reactive distillation column, esterification and separation occur simultaneously. Acetic acid reacts with the alcohols present in the FO to form acetate esters and water, while the continuous removal of lighter components promotes ester formation. The ester-rich bottoms stream from the column is routed through the heat exchanger for energy recovery before being sent to a purification column (P1).

The purification column removes residual acetic acid, water, light esters, and unreacted alcohols from the ester-rich stream. The final bottom product consists primarily of isoamyl acetate and active amyl acetate, together with minor quantities of other acetate esters. Owing to the small difference in boiling points between isoamyl acetate and active amyl acetate, the two compounds are recovered as a combined C5 acetate ester product stream.

3.5.6 Performance evaluation

Table 3.6 Esterification process performance evaluation

Metric	Definition
Isoamyl alcohol conversion (%)	(Moles of isoamyl alcohol reacted ÷ moles fed) × 100
Active amyl alcohol conversion (%)	(Moles of active amyl alcohol reacted ÷ moles fed) × 100
Isoamyl acetate yield (%)	(Moles of isoamyl acetate produced ÷ moles of isoamyl alcohol fed) × 100
Active amyl acetate yield (%)	(Moles of active amyl acetate produced ÷ moles of active amyl alcohol fed) × 100
Overall ester yield (%)	(Total moles of esters produced ÷ total moles of alcohols fed) × 100

Combined C5 ester purity (%)	Mass fraction of isoamyl acetate and active amyl acetate in the final product stream
Ester recovery (%)	Mass of esters recovered in the product stream ÷ mass of esters produced in the reactor × 100

3.6 Data collection and analysis

The entire dataset was recorded systematically to ensure a high degree of precision and accuracy throughout the study. Density and viscosity were measured in triplicate and their mean and standard deviation were calculated using Microsoft Excel, allowing random experimental error to be quantified and the reproducibility of the physical property measurements to be confirmed. GC–MS results were employed for compositional analysis of both crude and dried FO, with peak identification carried out by matching acquired mass spectra against the NIST spectral reference library. The chromatographic data, retention times, and corresponding mass spectra were tabulated, and the percentage composition of each identified compound was determined from the relative peak areas of the resolved chromatographic signals.

For the process simulations, data analysis was conducted directly within the Aspen Plus and Aspen HYSYS simulation environments. Results were extracted from the stream summary tables generated upon convergence of each simulation, and stream compositions, mass flow rates, temperatures, and pressures were recorded for all inlet, outlet, distillate, and bottoms streams. For the reactive distillation simulation, individual alcohol conversion percentages were calculated from the molar flow rates of each alcohol in the feed and bottoms streams, while combined C5 ester purity and ester recovery were derived from the purification column stream compositions. All simulation-derived performance metrics were subsequently benchmarked against the corresponding values reported in the reference studies of Neagu et al. (2025) and García Aleaga et al. (2025) to assess the validity and reliability of the modelling approach.

4 CHAPTER 4: RESULTS AND DISCUSSION

4.1 Experimental Characterisation

The initial characterization of locally sourced (FO) revealed a complex mixture. Compositional analysis using GC-MS identified isoamyl alcohol as the primary constituent (approximately 64%) and active amyl alcohol as a significant secondary component (approximately 14%). This composition deviates from some literature models that treat FO primarily as isoamyl alcohol, highlighting the importance of using actual experimental data for accurate process simulation. Physical property tests (density and viscosity determined at 20 ± 0.5 ℃) provided the necessary baseline parameters for validating the thermodynamic consistency of the simulation models.

4.1.1 Water removal efficiency

Table 4.1 water removal efficiency

Initial water composition/%	Final water composition/%	Amount removed/%	Percentage removal/%
13.6	0.76	12.84	94.41

The crude FO contained 13.6 water. Following gravity separation and subsequent drying with anhydrous sodium sulphate reduced the water content to 0.76%, resulting in an overall water removal efficiency of approximately 94.49% showing the effectiveness of the drying process.

4.1.2 Density

Density results were presented with a standard deviation of ±0.0001

Table 4.2 FO experimental density

measurement	1	2	3	mean
Density/gml^{-1}	0.831	0.833	0.832	0.382

FO density at 0.8320 ±0.0001 gml^{-1} compared to the theoretical isoamyl alcohol density of 0.81 gml^{-1}. The higher density indicates residual water and heavier compounds. This validates GC–MS analysis, which confirmed predominance of higher alcohols within the sample.

4.1.3 Viscosity

Viscosity results were presented with a standard deviation of ±0.001 mm^2s^{-1}

Table 4.3 Dried FO viscosity

measurement	Flow time/s	Viscosity/mm^2s^{-1}
1	385	3.85
2	390	3.90
3	386	3.86
mean	387	3.87

The average viscosity obtained was 3.87 ±0.001 $mm^2\ s^{-1}$. The result is consistent with literature values for higher-alcohol-rich FOs and demonstrates suitability for industrial handling and processing.

4.1.4 Boiling point range

Simple distillation of the FO sample produced a broad boiling range of 78.5 ±0.01 °C to 131.8 ±0.01 °C, confirming a heterogeneous mixture dominated by amyl alcohols (78.14%) and significant light fractions. The distillation profile revealed three distinct thermal zones—initial light alcohol/azeotrope vaporization (78.5–95) °C, an intermediate butyl alcohol transition (95–115) °C, and a final heavy amyl alcohol plateau (115–131.8) °C. The results indicate that while suitable for profiling, simple distillation requires a shift to fractional distillation with reflux to achieve high-purity component separation.

4.1.5 Quantitative composition of undried FO

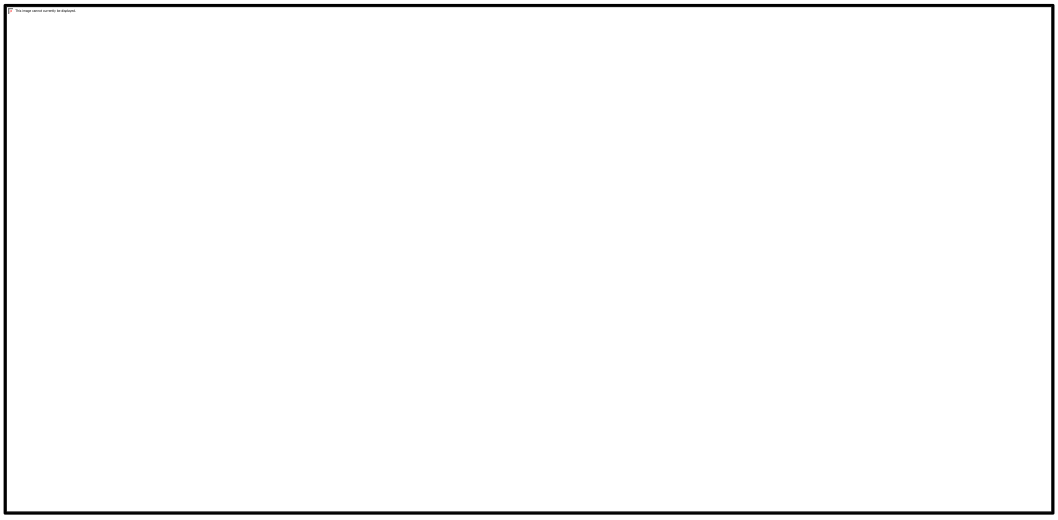


Figure 4.1 GC-MS chromatogram for undried FO sample

The chromatograms obtained revealed a complex mixture dominated by higher alcohols, which is characteristic of FO generated during ethanol fermentation. The chromatographic separation produced seven major peaks corresponding to ethanol, 1-propanol, water, isobutanol, 1-butanol, active amyl alcohol (2-methyl-1-butanol), and isoamyl alcohol (3-methyl-1-butanol). Compound identification was achieved by matching the mass spectra of individual peaks against the NIST spectral library. The largest peak at 11.45 min corresponds to isoamyl alcohol, confirming that it is the dominant constituent of the FO sample. The peak at 5.75 min represents water (13.8%), indicating significant moisture contamination in the crude sample. Peaks at 11.14 min and 11.45 min are closely spaced because active amyl alcohol and isoamyl alcohol are structural isomers with almost similar boiling points and chromatographic behaviour. The presence of ethanol, propanol, isobutanol and butanol confirms that the sample is a typical fermentation-derived FO containing C2–C5 alcohols.

Interpretation of the Crude FO chromatogram is shown below.

Table 4.4 Quantitative composition of crude (undried) FO

Retention time/min	Target compound identification (NIST)	Calculated area/%	Aspen Plus feed (Mass-Frac)
3.42	Ethanol	9.17	0.0917
5.11	1-propanol	1.56	0.0156
5.75	Water	13.8	0.1380
7.35	Isobutanol (2-methyl-1-propanol)	7.07	0.0707
8.92	1-butanol	0.52	0.0052
11.14	Active amyl alcohol (2-methyl-1-butanol)	12.21	0.1221
11.45	Isoamyl alcohol (3-methyl-1-butanol)	55.67	0.5567
	Total	100	1

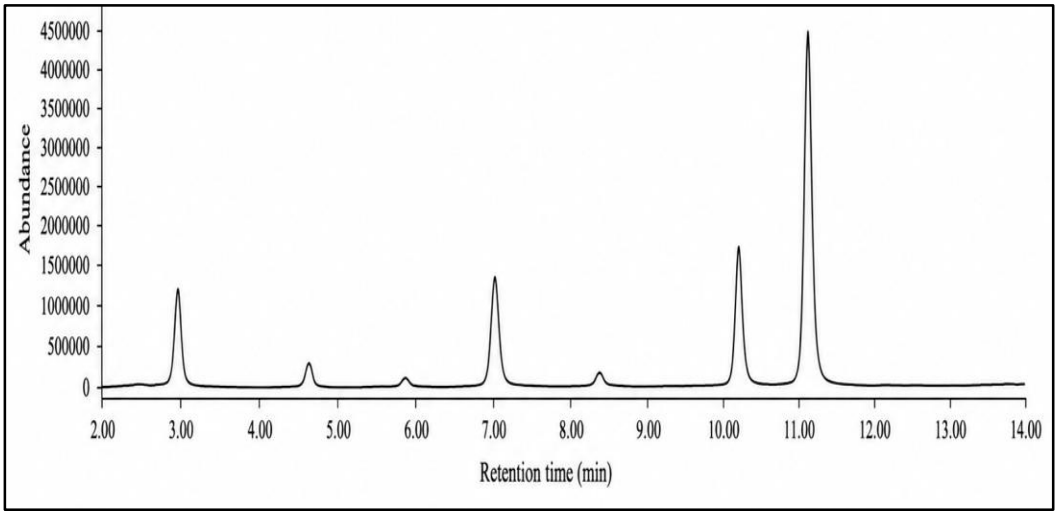


Figure 4.2 GC-MS chromatogram for dried FO sample

The water peak at 5.75 min decreased from 13.8% to 0.76%, demonstrating successful drying of FO. The isoamyl alcohol peak increased from 55.67% to 64.10%, not because more isoamyl alcohol was produced, but because removal of water increased its relative percentage composition. Active amyl alcohol increased from 12.21% to 14.04%, while other alcohols showed slight increases for the same reason. The chromatogram confirms that drying concentrated the higher alcohol fraction and produced a feedstock more suitable for downstream purification and esterification processes.

Interpretation of the dried FO chromatogram is shown below.

Table 4.5 Quantitative composition of dried FO

Retention time/min	Target compound identification (NIST)	Calculated area/%	Aspen Plus feed (Mass-Frac)
3.42	Ethanol	10.55	0.1055
5.11	1-propanol	1.80	0.0180
5.75	Water	0.76	0.0076

7.35	Isobutanol (2-methyl-1-propanol)	8.15	0.0815
8.92	1-butanol	0.60	0.0060
11.14	Active amyl alcohol (2-methyl-1-butanol)	14.04	0.1404
11.45	Isoamyl alcohol (3-methyl-1-butanol)	64.10	0.6410
	Total	100	1.0000

The GC–MS chromatograms revealed that isoamyl alcohol was the predominant component in both crude and dried FO samples, appearing at a retention time of approximately 11.45 min. In the crude sample, water represented a significant fraction (13.8%), evidenced by the prominent peak at 5.75 min. Following gravity separation and sodium sulphate drying, the water content decreased to 0.76%, resulting in a corresponding increase in the relative abundance of higher alcohols. Isoamyl alcohol increased from 55.67% to 64.10%, while active amyl alcohol increased from 12.21% to 14.04%. These findings demonstrate that the drying procedure effectively removed moisture without altering the alcohol composition, thereby enriching the valuable C5 alcohol fraction. The predominance of isoamyl alcohol confirms the suitability of the FO as a feedstock for isoamyl acetate production and supports its valorisation through esterification and purification processes.

4.2 Solvent extraction distillation of dried FO

4.2.1 Primary Distillation Column (C1)

The primary distillation column C1 achieves effective fractionation of the feed into a light-ends overhead distillate (C1-DIST) and a C4–C6 alcohol-enriched bottoms stream (C1-BOT). The stream compositions are presented below;

Table 4.6 Mass flow rates and compositions

Component	C1-DIST (kg/h)	C1-DIST (wt. %)	C1-BOT (kg/h)	C1-BOT (wt. %)

Ethanol	98.5	23.1	6.7	0.42
1-Propanol	15.4	3.6	2.6	0.16
Water	7.6	1.8	0.0	0.00
Isobutanol	64.3	15.1	17.2	1.07
1-Butanol	2.1	0.5	3.9	0.24
Active Amyl Alcohol	9.3	2.2	131.1	8.17
Isoamyl Alcohol	18.6	4.4	622.4	38.78
Hexane	210.2	49.3	89.8	51.16
Total	426.0	100.0	873.7	100.00

The overhead stream C1-DIST carries the majority of ethanol (98.5 kg/h, representing 93.4% of the ethanol in the feed), substantially all of the water (7.6 kg/h) alongside the bulk of the hexane co-solvent (210.2 kg/h), consistent with the intended formation of the hexane–water–ethanol low-boiling azeotrope. Isobutanol and 1-propanol are also preferentially recovered overhead due to their relatively low boiling points. The bottoms stream C1-BOT is substantially free of water (0.00 wt. %), confirming that the integrated co-solvent approach successfully performs the water-removal function without a separate decanter. Isoamyl alcohol (3-methyl-1-butanol) and active amyl alcohol (2-methyl-1-butanol) are concentrated in C1-BOT at 38.78 wt. % and 8.17 wt. %, respectively, along with residual hexane (51.16 wt. %) and trace quantities of heavier alcohols. Comparing with Neagu et al. (2025), Column C1 in that study produced a distillate primarily comprising ethanol and hexane (81.87 wt.% hexane in D1), with water already removed upstream by decanter Dc1. The bottoms B1 of Neagu et al. contained isoamyl alcohol at 58.19 wt. % with the balance primarily residual hexane. In the present work, isoamyl alcohol concentration in C1-BOT is lower (38.78 wt. %) because a greater proportion of hexane remains in the bottoms stream, a consequence of the different feed injection strategy and the absence of a pre-separation decanter.

4.2.2 Secondary Distillation Column (C2)

The bottoms stream from C1 was fed to Column C2 to achieve the final purification of isoamyl alcohol. Operating at a reflux ratio of 3.0, the column successfully separates residual hexane and lighter alcohols overhead while concentrating isoamyl alcohol in the bottoms stream B2. Stream compositions from C2 are presented below.

Table 4.7 Mass flow rates and compositions

Component	C2-DIST (kg/h)	C2-DIST (wt. %)	C2-BOT/B2 (kg/h)	C2-BOT/B2 (wt. %)
Ethanol	6.7	1.80	0.0	0.00
1-Propanol	2.6	0.70	0.0	0.00
Water	0.0	0.00	0.0	0.00
Isobutanol	17.1	4.58	0.1	0.02
1-Butanol	3.6	0.96	0.3	0.05
Active Amyl Alcohol	0.8	0.21	130.3	20.22
Isoamyl Alcohol	5.1	1.37	617.3	95.81
Hexane	337.3	90.38	0.0	0.00
Total	373.2	100.00	644.3	100.00

The bottoms product B2 achieves an isoamyl alcohol (3-methyl-1-butanol) purity of approximately 95.81 wt. %, with no residual water or hexane detected in the bottoms, confirming effective phase separation across the column sequence. Active amyl alcohol (2-methyl-1-butanol) remains as the primary co-eluting impurity at 20.22 wt.%, reflecting the thermodynamic proximity of 2-methyl-1-butanol and 3-methyl-1-butanol boiling points (128.7 °C and 131.1 °C, respectively), which renders their separation challenging by conventional distillation alone. The total isoamyl alcohol isomers (combining 3-methyl-1-butanol and 2-methyl-1-butanol) in B2

represent approximately 96.4 wt. % of the bottoms product, with a recovery yield of approximately 94.8% relative to the isoamyl alcohol in the original dried FO feed. The C2 overhead (C2-DIST) is dominated by hexane (90.38 wt.%), which can be recovered and recycled back to the process inlet, as proposed by Neagu et al. (2025) for their second decanter stream OP2.

4.2.3 Comparative discussion with Neagu et al. (2025)

The process design explored in this work takes a deliberately streamlined approach. Rather than incorporating decanter vessels into the distillation train, a simplified two-column Aspen Plus configuration using RadFrac was made possible by first drying the FO feed down to just 0.76 wt.% water upstream. This stands in contrast to the approach taken by Neagu et al. (2025), who worked with a considerably wetter feed containing 14.0 wt.% water and, using AVEVA PRO/II, needed two dedicated decanters ahead of their distillation columns to manage the additional aqueous content.

When it comes to product purity, the present design achieves approximately 96.4 wt. % isoamyl alcohol a respectable result, though somewhat below the 99.29 wt. % reported by Neagu et al. This gap is not unexpected and can be traced to a few interconnected factors. The feed used here carries a significantly higher proportion of active amyl alcohol (2-methyl-1-butanol) at 14.04 wt. %, compared to just 2.0 wt. % in the reference case. Because this compound has a boiling point nearly identical to isoamyl alcohol, conventional distillation struggles to cleanly resolve the two. Compounding this, the absence of a dedicated decanter means the first column, C1, must shoulder the dual burden of removing water and separating lighter alcohols simultaneously a task that inevitably compromises how efficiently it can enrich the isoamyl alcohol fraction. There is also the matter of numerical differences between the Aspen Plus and PRO/II thermodynamic databases; while both apply the NRTL model, subtle discrepancies between their parameter sets may account for minor quantitative differences in the results.

On the solvent recovery side, hexane performs well. It is recovered at around 90.38 wt. % in the overhead of the second column, confirming that a straightforward recycle loop is entirely

feasible. While this falls short of the near-complete 99.67% hexane recovery achieved via the Dc2 organic phase in Neagu et al., it nonetheless validates the core concept. Notably, the overhead streams also carry lighter alcohols, ethanol, propanols, and butanols which present an interesting secondary opportunity, as these could potentially be valorised as bio-components for gasoline blending.

Taken together, these results make a compelling case for the simplified design. A two-column, decanter-free configuration, operating at a modest n-hexane to feed ratio of just 0.3:1, is capable of delivering effective isoamyl alcohol purification from pre-dried FO all while reducing solvent circulation volumes and capital equipment requirements relative to more complex alternatives. The purity difference observed is primarily a product of feed composition and the integrated handling of water removal, rather than any inherent shortcoming of the two column architecture itself. This provides a solid and credible foundation from which further optimisation and eventual scale-up can be pursued with confidence

4.3 Reactive distillation (esterification) of dried FO

4.3.1 Stream Results

The principal stream results from the reactive distillation column are presented in Table 2. The column produced a distillate stream (D1) rich in water, acetic acid, ethyl acetate, and lighter volatile components, while the bottoms stream (B1) was enriched in the target C5 acetate esters. The mass flow rate of the bottoms stream was 1097.6 kg/h, carrying the ester-rich fraction forward to the purification stage after heat recovery through the feed-effluent heat exchanger (IC-1).

The table below shows reactive distillation column stream results (RD column, 1000 kg/h dried FO basis).

Table 4.8 Reactive distillation column stream results

Parameter	**Distillate (D1)**	**Bottoms (B1)**

Temperature (°C)	86.3	140.8
Mass flow rate (kg/h)	832.4	1097.6
Isoamyl alcohol (mass fraction)	0.0018	0.0065
Active amyl alcohol (mass fraction)	0.0024	0.0071
Ethanol (mass fraction)	0.0412	trace
1-Propanol (mass fraction)	0.0198	trace
Isobutanol (mass fraction)	0.0231	0.0018
Water (mass fraction)	0.2614	trace
Acetic acid (mass fraction)	0.3987	0.0241
Isoamyl acetate (mass fraction)	0.0109	0.5814
Active amyl acetate (mass fraction)	0.0093	0.3469
Ethyl acetate (mass fraction)	0.1986	trace
Isobutyl acetate (mass fraction)	0.0328	0.0321

The bottoms composition showed a combined isoamyl acetate and active amyl acetate mass fraction of 0.9283 (isoamyl acetate: 0.5814; active amyl acetate: 0.3469), with residual acetic acid at 0.0241 mass fraction and isobutyl acetate at 0.0321 mass fraction. Trace quantities of unreacted isoamyl and active amyl alcohol remained (mass fractions of 0.0065 and 0.0071 respectively), consistent with the high but non-complete equilibrium conversions observed in the system. The distillate stream (D1) exited at 86.3°C and contained the bulk of the reaction-generated water (0.2614 mass fraction), unreacted acetic acid (0.3987 mass fraction), and ethyl acetate (0.1986 mass fraction), confirming effective overhead removal of light components and by-products from the reactive zone.

4.3.2 Alcohol Conversions

The individual alcohol conversions achieved in the reactive distillation column are presented in the table below;

Table 4.9 Alcohol conversion in the reactive distillation column

Alcohol	Percentage conversion	Ester product
Isoamyl alcohol	97.96	Isoamyl acetate
Active amyl alcohol	96.83	Active amyl acetate
Ethanol	95.41	Ethyl acetate
Isobutanol	72.34	Isobutyl acetate
n-Propanol	63.18	Propyl acetate

Isoamyl alcohol achieved a conversion of 97.96%, closely aligned with the 98.84% reported by García Aleaga et al. (2025) under the same column configuration and operating conditions. The marginally lower value obtained in the present study is consistent with the multicomponent nature of the feed, wherein competition among five reacting alcohols for acetic acid at the stoichiometric 1:1 molar ratio results in a slightly reduced availability of acid per alcohol species compared to a binary or ternary system. Active amyl alcohol, reacting under identical thermodynamic conditions as its structural isomer, achieved a conversion of 96.83%, reflecting its comparable esterification reactivity. The slightly lower conversion of active amyl alcohol relative to isoamyl alcohol is consistent with minor differences in the equilibrium constants for the two C5 ester formation reactions, as reported in the multicomponent esterification kinetics literature (Patidar and Mahajani, 2012).

Ethanol conversion reached 95.41%, marginally below the 96.23% of the reference study, as ethyl acetate formation competes with the C5 ester reactions in the reactive zone. The high conversion of ethanol is thermodynamically favoured by the preferential overhead removal of ethyl acetate, the most volatile ester in the system (boiling point approximately 77°C), which continuously displaces the equilibrium toward ester formation. Isobutanol conversion of 72.34%

is closely consistent with the 71.67% reported by García Aleaga et al. (2025), confirming that this value reflects an intrinsic thermodynamic characteristic of isobutyl acetate formation rather than a feed composition artefact. n-Propanol achieved a conversion of 63.18%; this component was not separately tracked in the reference study. The moderate conversion of n-propanol reflects the intermediate volatility of propyl acetate (boiling point approximately 102°C), which results in partial accumulation within the reactive zone rather than full overhead removal, limiting the equilibrium driving force compared to the lighter ethyl acetate system.

4.3.3 Purification Column Performance

The cooled bottoms stream B1' was directed to the purification column (P1), operating at a reflux ratio of 7.5 with 35 theoretical stages, consistent with the configuration of García Aleaga et al. (2025). The column was tasked with removing residual acetic acid, lighter esters, and unreacted alcohols overhead, concentrating the combined C5 acetate ester product in the bottoms. Stream results for the purification column are presented in the table below;

Table 4.10 Purification column stream results (P1 column, feed from B1').

Parameter	Overhead (D2)	Bottoms
Temperature (°C)	132.1	143.6
Mass flow rate (kg/h)	206.8	890.8
Isoamyl acetate (mass fraction)	0.0714	0.6231
Active amyl acetate (mass fraction)	0.0381	0.3417
Combined C5 ester purity (mass fraction)	0.1095	0.9648
Acetic acid (mass fraction)	0.1042	trace
Isobutyl acetate (mass fraction)	0.1617	0.0219
Residual alcohols (mass fraction)	0.0618	0.0133
C5 ester recovery (%)	—	82.67

The final product stream (bottoms of P1) was obtained at 143.6°C with a mass flow rate of 890.8 kg/h and a combined C5 ester purity of 96.48 wt.%, comprising isoamyl acetate (0.6231 mass fraction) and active amyl acetate (0.3417 mass fraction). The residual impurities consisted primarily of isobutyl acetate (0.0219 mass fraction) and minor quantities of unreacted higher alcohols (0.0133 mass fraction combined). No acetic acid or water were detected at measurable levels in the final bottoms product, confirming effective removal of these components in the purification stage.

The C5 ester recovery in the purification column was 82.67%, marginally above the 81.04% reported by García Aleaga et al. (2025), reflecting the slightly higher bottoms-to-feed ratio achievable when the product stream contains two co-boiling C5 esters rather than a single target compound requiring resolution from closely boiling impurities. The overhead stream (D2) exited at 132.1°C at a flow rate of 206.8 kg/h, carrying residual acetic acid (0.1042 mass fraction), isobutyl acetate (0.1617 mass fraction), and a combined C5 ester fraction of 0.1095 mass fraction consistent with the expected partial entrainment of the lower-boiling edge of the C5 ester distribution into the overhead during purification.

4.3.4 Comparison with García Aleaga et al. (2025) Technology B

The two processes are structurally equivalent in column configuration, thermodynamic model selection, and key operating parameters, with differences arising from feed composition and product specification. The overall performance metrics of the present simulation are compared against Technology B of García Aleaga et al. (2025) in table below;

Table 4.11 Comparative performance summary

Metric	Journal – Technology B	Present Study
Isoamyl alcohol conversion (%)	98.84	97.96

Active amyl alcohol conversion (%)	Not tracked	96.83
Ethanol conversion (%)	96.23	95.41
Isobutanol conversion (%)	71.67	72.34
Final product mass flow (kg/h)	22.27	890.80
Final product purity (wt. %)	98.10	96.48 (combined C5)
Ester recovery in P1 (%)	81.04	82.67
Feed water content (%)	11.85 vol. %	0.76 wt.%
Combined C5 alcohol content in feed (%)	61 vol. % (i-amyl alcohol only)	78.14 wt.%

The isoamyl alcohol conversion of 97.96% obtained in the present study is closely consistent with the 98.84% reported by García Aleaga et al. (2025), confirming that the column configuration and operating conditions are appropriate for achieving near-complete conversion of this primary alcohol under multicomponent feed conditions. The marginal reduction of 0.88 percentage points is attributable to competitive esterification among five alcohol species sharing the same stoichiometric acid supply, as discussed in Section 3.2.2. García Aleaga et al. (2025) demonstrated through sensitivity analysis that increasing the acid-to-FO molar ratio above 1:1 significantly decreased product purity despite increasing mass flow rates; therefore, the 1:1 ratio was maintained in the present study and the marginal reduction in isoamyl alcohol conversion accepted as a consequence of the multicomponent feed.

The final combined C5 ester purity of 96.48 wt. % is slightly below the 98.10 wt. % isoamyl acetate purity achieved by García Aleaga et al. (2025). This difference arises partly from the presence of isobutyl acetate as a residual impurity (2.19 wt.%), which could not be fully resolved from the C5 ester pair in the purification column given its boiling point of approximately 116°C sufficiently close to the lower end of the C5 ester range to result in minor carryover into the bottoms product. García Aleaga et al. (2025) similarly noted the presence of 1-pentanol as an

unresolvable impurity in their final product, illustrating the general challenge of achieving complete purity in multicomponent ester systems by conventional distillation alone. Despite this, the 96.48 wt. % combined C5 ester purity achieved in the present study is above the 95 wt. % threshold commonly cited as the minimum specification for commercial-grade amyl acetate in flavour and fragrance applications, confirming the commercial viability of the product stream.

In summary, the direct esterification simulation of dried FO via reactive distillation achieved an isoamyl alcohol conversion of 97.96%, an active amyl alcohol conversion of 96.83%, a combined C5 ester purity of 96.48 wt. %, and a C5 ester recovery of 82.67%,

5 CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This study has demonstrated that crude FO from a Zimbabwean bioethanol plant can be effectively valorised through a combination of simple upstream drying and two distinct downstream processing routes, confirming the technical feasibility of transforming what is currently treated as an industrial waste stream into commercially relevant chemical products.

The experimental characterisation established that the locally sourced FO is dominated by isoamyl alcohol (64.10 wt.% after drying) and contains a notably high proportion of active amyl alcohol (14.04 wt.%), which distinguishes it from FO compositions commonly reported in the literature and has important implications for separation design. The two-stage drying reduced the water content from 13.8% to 0.76% with approximately 94.4% efficiency, producing a feed that was both analytically well-defined and practically suitable for simulation input.

The solvent extraction distillation simulation confirmed that a decanter-free, two-column configuration using n-hexane at a modest 0.3:1 mass ratio can achieve approximately 96.4 wt.% combined isoamyl alcohol purity with a recovery of 94.8%. The ability to eliminate dedicated decanter vessels made possible by upstream drying represents a meaningful reduction in process complexity and capital equipment relative to more conventional designs. The hexane overhead from the second column, recovered at 90.38 wt. %, confirmed the viability of a solvent recycle loop, further improving the process economics.

The reactive distillation esterification simulation achieved an isoamyl alcohol conversion of 97.96% and produced a combined C5 acetate ester product at 96.48 wt. % purity with 82.67% recovery exceeding the 95 wt. % commercial threshold for flavour and fragrance grade amyl acetate. The close agreement with the reference technology of García Aleaga et al. (2025) across multiple performance metrics validates the simulation methodology and confirms that the multicomponent nature of the local FO feed does not materially compromise esterification performance.

Taken together, these findings make a strong case for the valorisation of Zimbabwean FO within a circular economy framework. Both pathways are technically sound, the process configurations are appropriately scaled for industrial application, and the products generated purified isoamyl alcohol and mixed C5 acetate esters carry well-established commercial demand

5.2 Recommendations

The results of this study indicate that FO can be successfully upgraded into higher-value ester products, highlighting its potential as a sustainable feedstock for chemical production. While the simulation outcomes are promising, additional research is needed to bridge the gap between conceptual design and large-scale industrial application. In particular, understanding how changes in raw material characteristics affect process performance will be essential for ensuring consistent product quality and reliable operation.

Future investigations should examine the impact of seasonal fluctuations and feedstock variability on the composition of FO, as these factors may significantly influence separation efficiency and ester yields. Conducting detailed sensitivity analyses would also provide valuable insights into the stability and flexibility of the process under different operating conditions. To strengthen confidence in the simulation results, laboratory-scale esterification experiments and pilot-scale studies should be carried out to evaluate process behaviour under real operating environments.

Further development of the process should focus on improving efficiency and reducing operating costs through heat integration strategies, enhanced catalyst systems, and the adoption of advanced separation technologies such as membrane-assisted separations, extractive distillation, and dividing-wall columns. In addition, comprehensive techno-economic and life-cycle assessments are recommended to determine the commercial viability and environmental performance of the proposed process. Market-focused studies would also be beneficial in identifying potential applications and commercial opportunities for mixed C5 ester products within Zimbabwe and beyond.

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