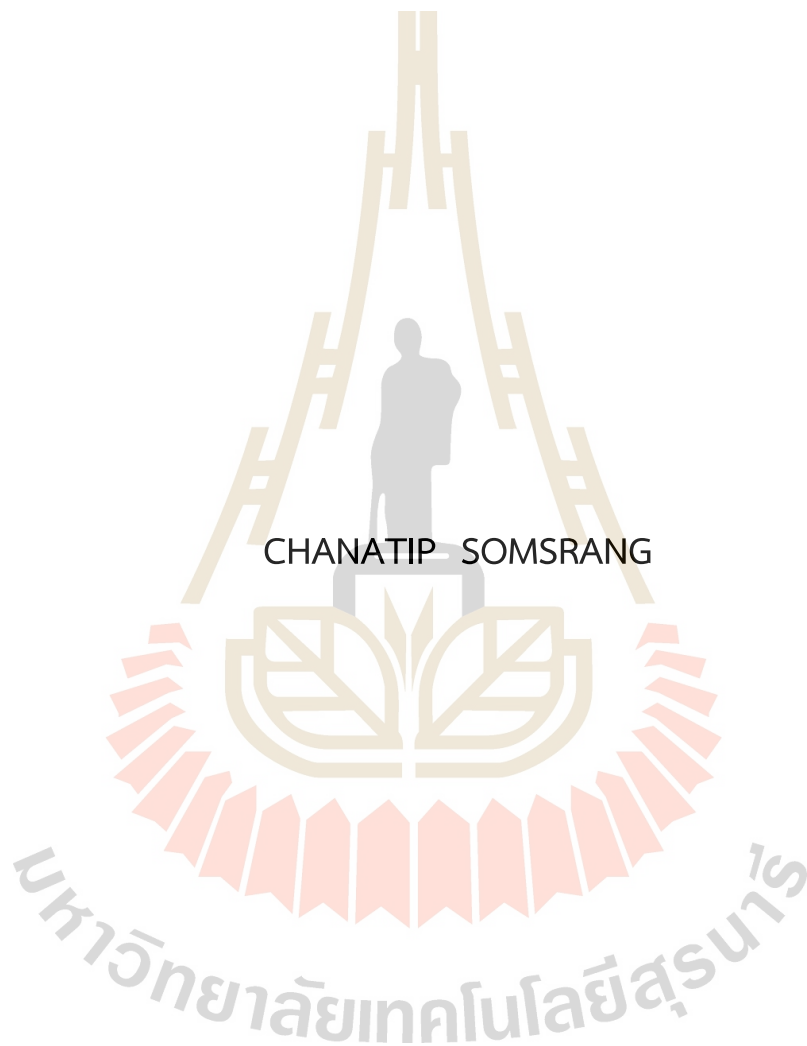


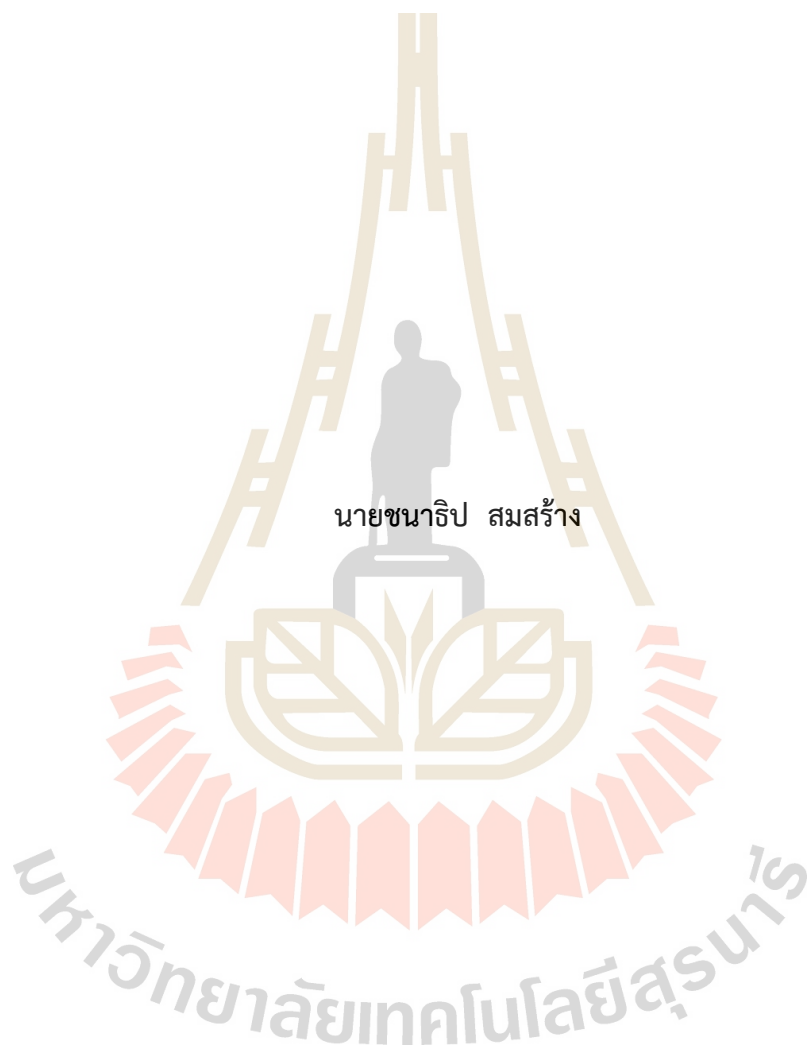
FEASIBILITY STUDY OF PILOT SCALE SYNTHESIS OF ISO-AMYL
ACETATE USING REACTIVE DISTILLATION TECHNIQUE



CHANATIP SOMSRANG

A Thesis Submitted in Partial Fulfillment of the Requirements for the
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Suranaree University of Technology
Academic Year 2024

การศึกษาความเป็นไปได้ในการสังเคราะห์ไอโซเอมิลอะซีเตทในระดับโรงงานต้นแบบด้วยเทคนิค
การกลั่นแบบมีปฏิริยา



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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FEASIBILITY STUDY OF PILOT SCALE SYNTHESIS OF ISO-AMYL ACETATE USING REACTIVE DISTILLATION TECHNIQUE

Suranaree University of Technology has approved this thesis submitted in partial fulfillment of the requirements for a Master's Degree.

Thesis Examining Committee



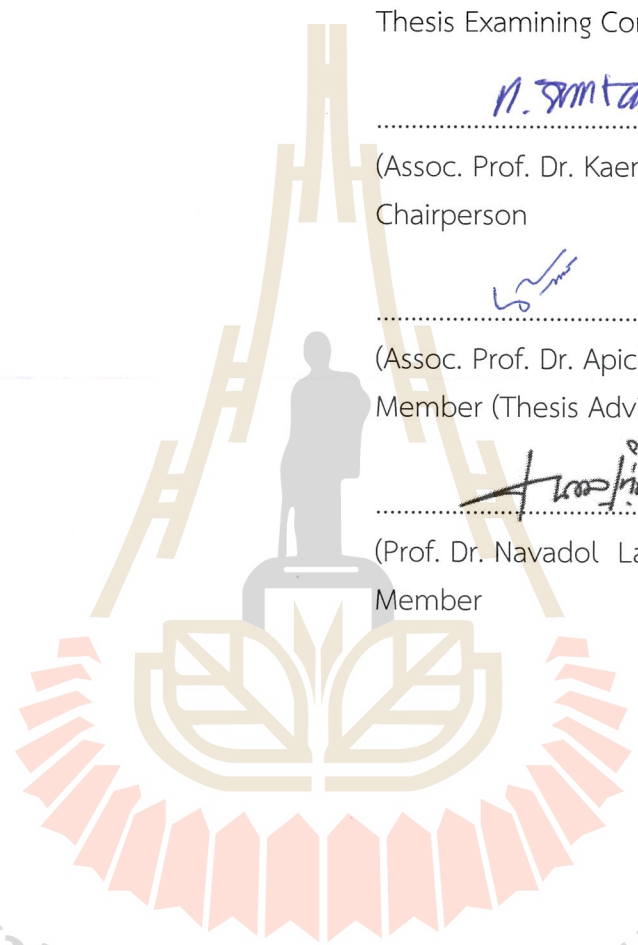
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คำสำคัญ: ไอโซเอมิลอะซิเตท/ฟูเซลออยล์/การกลั่นแบบมีปฏิกิริยา/การเพิ่มประสิทธิภาพ

โครงการวิจัยนี้มีเป้าหมายในการพัฒนากระบวนการผลิตสารเอสเทอร์ชนิด isoamyl acetate จาก fusel oil ซึ่งเป็นผลพลอยได้จากการหมักเอทานอล เพื่อยกระดับของเหลือทิ้งในอุตสาหกรรมเอทานอลให้มีมูลค่าเพิ่มและสามารถนำไปใช้ในอุตสาหกรรมอาหาร น้ำหอม และสารปรุงแต่งกลิ่นรสต่าง ๆ โครงการนี้เกิดจากความร่วมมือระหว่างมหาวิทยาลัยเทคโนโลยีสุรนารีและบริษัท เคทิส ไปโอเอทานอล จำกัด โดยมุ่งศึกษาและทำความเข้าใจปัจจัยด้านวิศวกรรมที่มีผลต่อประสิทธิภาพของกระบวนการ โดยให้ความสำคัญกับเทคโนโลยีการกลั่นแบบมีปฏิกิริยา ซึ่งช่วยเพิ่มอัตราการเปลี่ยนและลดขั้นตอนการแยกสารในกระบวนการผลิต

ขั้นตอนแรกคือการกลั่น fusel oil ด้วยระบบกลั่นลำดับส่วนระดับโรงงานต้นแบบที่รองรับสารป้อนได้ 100 ลิตรต่อวัน โดยให้ isoamyl alcohol ความบริสุทธิ์ 99.61% และ recovery 95.63% จากนั้นจึงนำไปทำปฏิกิริยาเอสเทอริฟิเคชันกับกรดอะซิติก โดยใช้ตัวเร่งปฏิกิริยา Amberlyst 15E ภายใต้ระบบกลั่นแบบมีปฏิกิริยา ซึ่งสามารถกำจัดน้ำทันทีและทำให้ได้ conversion สูงสุด 100% ในเวลาเพียง 8 ชั่วโมง นอกจากนี้ยังมีการศึกษาแบบจำลองจลนพลศาสตร์และสมดุลวัฏภาคด้วยวิธี NRTL และ UNIFAC เพื่อนำไปสู่การออกแบบกระบวนการที่แม่นยำ ผลการทดลองสามารถผลิต isoamyl acetate ได้ประมาณ 60 กิโลกรัมต่อวัน มีความบริสุทธิ์มากกว่า 99% พร้อมทั้งวิเคราะห์สมดุลมวล พลังงาน และความคุ้มค่าทางเศรษฐศาสตร์ เพื่รองรับการพัฒนาในระดับอุตสาหกรรมต่อไป

สาขาวิชาเทคโนโลยีชีวภาพ

ปีการศึกษา 2568

ลายมือชื่อนักศึกษาชนาธิป.....

ลายมือชื่ออาจารย์ที่ปรึกษา.....

CHANATIP SOMSRANG: FEASIBILITY STUDY OF PILOT SCALE SYNTHESIS OF
ISO-AMYL ACETATE USING REACTIVE DISTILLATION TECHNIQUE.

THESIS ADVISOR: ASSOC. PROF. APICHAT BOONTAWAN, Ph.D. 72 PP.

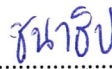
Keyword: Isoamyl acetate/Fusel oil/Reactive distillation/Process optimization

This research project aims to develop an efficient process for producing isoamyl acetate from fusel oil, a by-product of ethanol fermentation. The objective is to add value to waste streams from the ethanol industry by converting them into high-value ester products used in food, fragrance, and flavor applications. Conducted through collaboration between Suranaree University of Technology and KTIS Bioethanol Co., Ltd., the study focuses on engineering and technical factors that influence process performance, with particular emphasis on reactive distillation, which integrates reaction and separation into a single unit to improve overall efficiency. The first stage involves fractional distillation of fusel oil using a pilot-scale unit capable of processing 100 liters per day, producing isoamyl alcohol with 99.61% purity and 95.63% recovery. The purified alcohol is esterified with acetic acid using Amberlyst 15E under reactive distillation conditions, allowing continuous removal of water and resulting in conversion up to 100% within 8 hours. Reaction kinetics and VLE models (NRTL and UNIFAC) were also developed to support accurate simulation and optimization.

The system produced approximately 60 kg per day of isoamyl acetate with over 99% purity. Economic and energy analyses confirmed the feasibility of commercial-scale implementation.

School of Biotechnology

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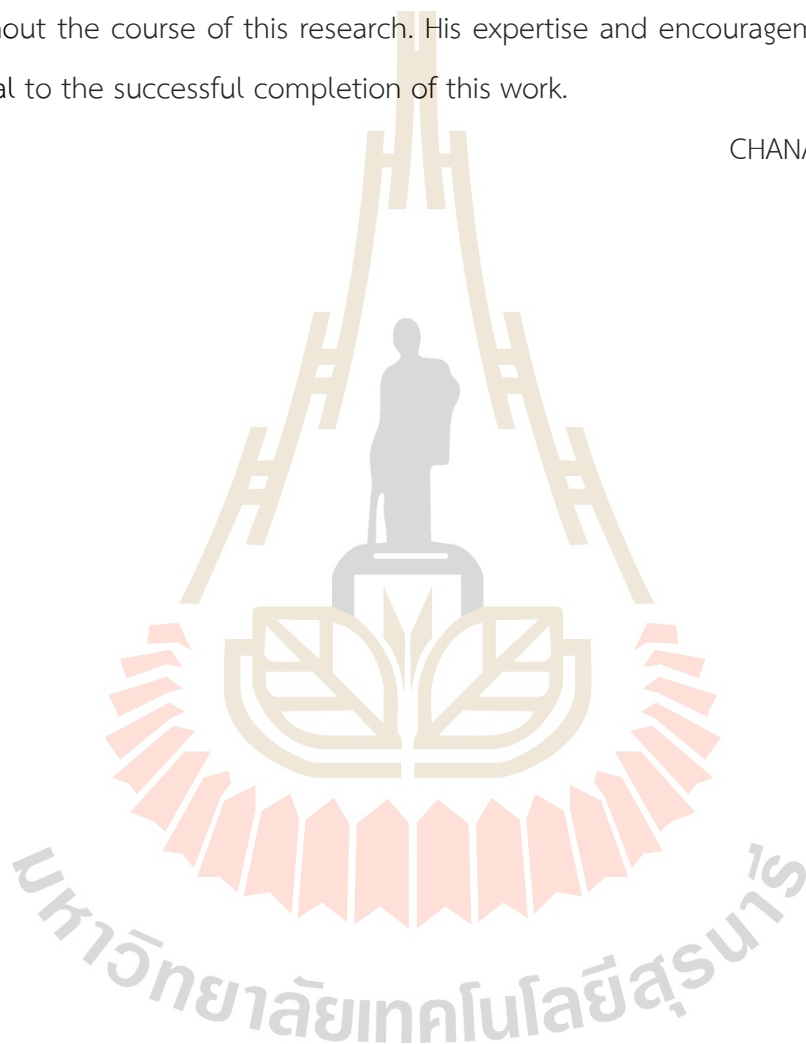
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LIST OF ABBREVIATIONS

AA	Acetic Acid
AM	BERLYSTTM 15E Macroporous sulfonic acid ion-exchange resin catalyst
Aspen Plus	Process simulation software for chemical engineering
BP	Boiling Point
CAPEX	Capital Expenditure
FID	Flame Ionization Detector
GC	Gas Chromatography
GC-FID	Gas Chromatography with Flame Ionization Detection
IAAc	Isoamyl Acetate
IAA	Isoamyl Alcohol
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectroscopy
NRTL	Non-Random Two-Liquid model (thermodynamic model)
RD	Reactive Distillation
SP	Structured Packing
SUT	Suranaree University of Technology
UNIFAC	UNIQUAC Functional-Group Activity Coefficients model
UNIQUAC	Universal Quasi-Chemical model
VLE	Vapor-Liquid Equilibrium

CHAPTER I

INTRODUCTION

1.1 Introduction

The expansion of the bioethanol industry has led to a parallel increase in the generation of fusel oil, a low-value by-product composed of higher alcohols such as isoamyl alcohol, iso-butanol, and propanol. Disposal or underutilization of fusel oil presents both environmental and economic challenges, prompting interest in valorization strategies that convert this residue into higher-value chemicals. Isoamyl acetate, commonly known for its banana-like aroma, is an ester widely used in the food, fragrance, and solvent industries. Its global demand continues to grow, driven by applications in flavoring, perfumery, coatings, and green solvents, with Asia-Pacific occupying the largest market share. Conventionally, isoamyl acetate is synthesized from petrochemical routes; however, sustainable production from renewable feedstocks is increasingly sought to align with circular economy principles and environmental regulations.

In this context, fusel oil from bioethanol plants provides a promising renewable source of isoamyl alcohol. By employing separation and purification steps followed by esterification with acetic acid, fusel oil can be upgraded into isoamyl acetate with significant value addition. This approach not only reduces waste but also generates economic benefits for bioethanol industries. To intensify this process, reactive distillation (RD) has been investigated as an alternative to conventional batch esterification. RD integrates reaction and separation in a single unit, overcoming equilibrium limitations, lowering energy demand, and simplifying downstream purification. Previous studies have reported improved yields, higher purities, and reduced environmental footprints compared with conventional routes. The present

study focuses on the pilot-scale production of isoamyl acetate from fusel oil, combining experimental batch screening of catalysts and operating parameters with mathematical modeling and Aspen Plus simulation of reactive distillation. The work aims to demonstrate both the technical feasibility advantages of valorizing fusel oil through process intensification, thereby contributing to sustainable bio-based chemical production.

1.2 Research Objectives

- 1.2.1 To investigate the feasibility of valorizing fusel oil
- 1.2.2 To identify suitable catalytic and operating conditions for esterification, with emphasis on heterogeneous resins.
- 1.2.3 To design and operate a pilot-scale reactive distillation process for isoamyl acetate production under optimized conditions.
- 1.2.4 To evaluate the technical performance of the integrated process through experimental trials and Aspen Plus simulation.

1.3 Scope of Research

1.3.1 Variability in Fusel Oil Composition

The composition of fusel oil varies significantly depending on the type of raw material, fermentation conditions, and ethanol production processes. In this study, fusel oil was sourced from a single industrial facility. As a result, the findings may not fully represent the compositional variability of fusel oil obtained from other production sites, which could influence separation behavior and overall process performance.

1.3.2 Limited Catalyst Evaluation at Pilot Scale

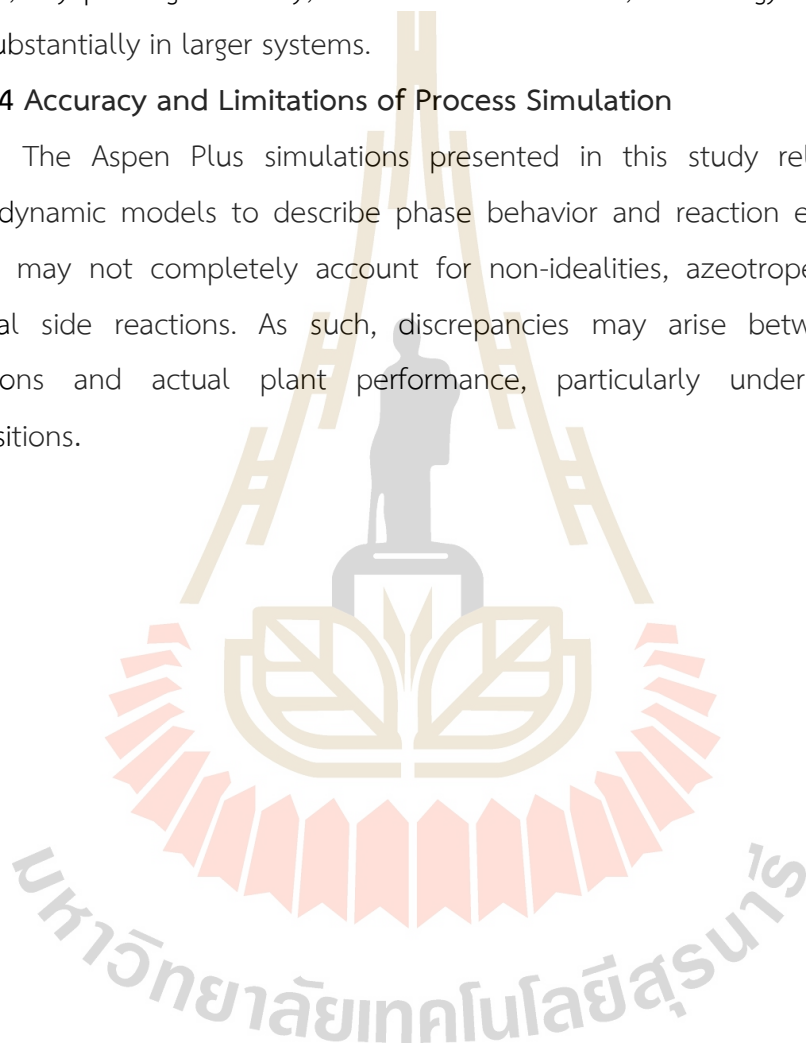
Although several heterogeneous catalysts—including Tulsion® resins and IND-190 were screened under laboratory conditions, comprehensive pilot-scale evaluation was conducted primarily using Amberlyst™ 15E. Consequently, while the study demonstrates the strong performance of Amberlyst™ 15E, the long-term stability, regeneration capability, and industrial feasibility of alternative catalysts remain unconfirmed.

1.3.3 Pilot-Scale Constraints and Industrial Scale-Up

All experimental work was carried out at the pilot scale, which provides valuable proof-of-concept and operational insight. However, pilot-scale systems may not fully capture the hydrodynamic behavior, energy requirements, and operational costs encountered at full industrial scale. Scale-up challenges such as non-ideal flow patterns, tray/packing efficiency, heat-transfer limitations, and energy optimization may differ substantially in larger systems.

1.3.4 Accuracy and Limitations of Process Simulation

The Aspen Plus simulations presented in this study rely on selected thermodynamic models to describe phase behavior and reaction equilibria. These models may not completely account for non-idealities, azeotrope formation, or potential side reactions. As such, discrepancies may arise between simulated predictions and actual plant performance, particularly under varying feed compositions.



CHAPTER II

LITERATURE REVIEW

2.1 Raw Material and Utilization of Iso-amyl Alcohol (IAA)

2.1.1 Composition of Fusel Oil

Fusel oil is a byproduct formed in small quantities during ethanol fermentation by yeast, mainly composed of higher alcohols (fusel alcohols), which are produced via the Ehrlich pathway and amino acid metabolism. Typically, fusel oil makes up only 0.2–0.5% of the total ethanol yield but poses a major quality concern in alcoholic beverages due to its unpleasant odor and flavor (Massa et al., 2023).

The primary components of fusel oil include:

- Iso-amyl alcohol (3-methyl-1-butanol, IAA): the most abundant, accounting for 50–70% of fusel oil depending on the yeast strain and fermentation conditions (Ferreira & Meirelles, 2013).
- Active amyl alcohol (2-methyl-1-butanol): approximately 10–20%
- Other alcohols such as n-butanol, hexanol, and esters in small amounts (Massa et al., 2023)

Industrially, iso-amyl alcohol (IAA) is the main target for extraction from fusel oil due to its higher market value compared to other fusel alcohols and its potential for conversion into various commercial chemicals (Ferreira & Meirelles, 2013).

2.2.2 Importance of Iso-amyl Acetate (IAAc)

Once purified, iso-amyl alcohol (IAA) can be converted into iso-amyl acetate (IAAc)—one of the most valuable products—through esterification with acetic acid (Torres et al., 2010). IAAc is highly valued for its strong banana-like aroma, making it an essential flavor compound in the food and beverage industries (Yilmaztekin et al., 2009). In addition to its use in flavoring, it is widely employed in the fragrance and cosmetic industries due to its sweet scent and high stability (Torres et al., 2010).

Furthermore, IAAC acts as a solvent for nitrocellulose, lacquers, and printing inks (Tran et al., 2020). It also serves as an intermediate plasticizer and has been studied as a biofuel additive, due to its compatibility with ethanol (Dias et al., 2020). The conversion of IAA into IAAC adds significant value, transforming fusel oil from an unwanted waste product into a high-value specialty chemical.

This chemical has strong demand, particularly in the flavor and fragrance industry, as well as in the green solvents market (Ali et al., 2009; Tran et al., 2020).

2.2.3 Thermodynamic Properties of Fusel Oil Components

The thermodynamic properties of fusel oil components are essential for understanding their separation, purification, and transformation processes. These properties — such as boiling point, density, vapor pressure, enthalpy of vaporization, and solubility — are critical for designing distillation and extraction units, as well as modeling vapor–liquid equilibrium (VLE) in multicomponent systems (Ferreira & Meirelles, 2013). Fusel oil is primarily composed of higher alcohols ranging from C3 to C6, each with distinct polarity, molecular weight, and volatility. These differences influence not only their odor and solubility but also the energy requirements for recovery and purification. For instance, iso-amyl alcohol (3-methyl-1-butanol) and iso-butanol (2-methyl-1-propanol) exhibit relatively high boiling points and moderate polarity, making their separation from ethanol and water challenging (Massa et al., 2023). From the thermodynamic standpoint, the components of fusel oil display progressively increasing boiling points and decreasing solubility as the carbon chain length increases. Lower alcohols such as n-propanol are completely miscible with water, whereas higher alcohols (iso-amyl alcohol, hexanol) show poor miscibility due to their hydrophobic nature (Massa et al., 2023). The enthalpy of vaporization rises with molecular weight, indicating stronger intermolecular interactions and higher energy requirements for vaporization. These properties are critical in designing multistage distillation or solvent extraction systems for industrial recovery of iso-amyl alcohol and other valuable components (Ferreira & Meirelles, 2013). Additionally, for modeling and simulation, thermodynamic data of these alcohols are typically correlated using activity coefficient models such as NRTL and UNIQUAC or equations of state.

Table 1. Physical and chemical properties.

Compound	Molecular Formula	Molar Mass (g·mol ⁻¹)	Boiling Point (°C)	Density (g·cm ⁻³ , 20°C)	Enthalpy of Vaporization (kJ·mol ⁻¹)	Water Solubility (g/100 g H ₂ O, 20°C)
Iso-amyl alcohol	C ₅ H ₁₂ O	88.15	131–132	0.81	52	2.0
iso amyl alcohol	C ₅ H ₁₂ O	88.15	128	0.81	50	1.8
Iso-butanol	C ₄ H ₁₀ O	74.12	108	0.802	45	8.5
N-Propanol	C ₃ H ₈ O	60.10	97	0.804	44	Miscible
n-Butanol	C ₄ H ₁₀ O	74.12	117.7	0.810	52	7.7
Hexanol	C ₆ H ₁₄ O	102.17	157	0.82	56	0.6
Iso-amyl acetate	C ₇ H ₁₄ O ₂	130.19	142	0.876	45	0.3

Additionally, for modeling and simulation, thermodynamic data of these alcohols are typically correlated using activity coefficient models such as NRTL and UNIQUAC or equations of state like Peng–Robinson for vapor–liquid equilibrium (Torres et al., 2010). Accurate property data enable optimization of energy consumption and product purity in fusel oil refining and esterification processes.

2.2 Separation and Purification Techniques of Iso-amyl Alcohol (IAA)

The recovery and purification of iso-amyl alcohol (IAA) from fusel oil is a crucial step in valorizing by-products from ethanol fermentation. Fusel oil is a complex multicomponent mixture containing various higher alcohols such as iso-butanol, n-propanol, active amyl alcohol, and other minor compounds with closely overlapping boiling points (97–132 °C). These components exhibit strong non-ideal behavior, forming azeotropes and complex vapor–liquid equilibria, which make separation and purification thermodynamically challenging (Ferreira & Meirelles, 2013; Wang et al., 2020). The goal of separation is to isolate high-purity IAA (>95%) suitable for further conversion into iso-amyl acetate (IAAc) or other specialty chemicals. Achieving this

requires advanced and energy-efficient techniques capable of overcoming azeotropic limitations, minimizing losses, and ensuring environmentally sustainable operation.

2.2.1 Methods of Separating Iso-amyl Alcohol (IAA) from Fusel Oil

Separating IAA from fusel oil cannot rely solely on simple distillation because most fusel alcohols have similar volatilities and often form azeotropes. Therefore, modern processes employ hybrid and intensified methods to improve purity, selectivity, and energy efficiency. The main techniques include:

- Simple Distillation: This is the most basic separation approach and is often used in laboratory-scale operations for preliminary concentration of fusel oil fractions. It exploits differences in boiling points; however, since iso-amyl alcohol (b.p. 131–132 °C) is close to that of iso-butanol (b.p. 108 °C) and n-propanol (b.p. 97 °C), the process suffers from overlapping vapor compositions and azeotrope formation (Pereira et al., 2011). As a result, distillates obtained through simple distillation rarely exceed 80–85% purity. Despite its simplicity, it remains useful for pre-treatment or partial fractionation before more selective methods are applied.
- Azeotropic or Extractive Distillation: Azeotropic and extractive distillation methods introduce entrainers or solvents to modify the relative volatility between components, thereby breaking azeotropes. Typical entrainers include water, glycerol, ethylene glycol, and more recently, ionic liquids (ILs). Souza et al. (2017) demonstrated that using ILs such as 1-butyl-3-methylimidazolium chloride significantly enhanced the selectivity of IAA separation while reducing environmental impact compared to traditional organic solvents. Ionic liquids offer negligible vapor pressure, high thermal stability, and tunable polarity, making them ideal for sustainable separation processes (Ferreira & Meirelles, 2013; Wang et al., 2020).
- Pressure Swing Distillation (PSD): Pressure Swing Distillation is an advanced technique that manipulates the vapor–liquid equilibrium (VLE) by altering the operating pressure between two or more columns. Changing pressure shifts the azeotropic composition, allowing separation of components that form azeotropes under atmospheric pressure. This method is especially effective for alcohol mixtures like IAA–isobutanol, achieving higher purities while reducing

reboiler energy consumption (Chen et al., 2023). Moreover, PSD minimizes solvent use and provides greater process flexibility, making it suitable for continuous industrial operation (Wang et al., 2020).

- Dividing Wall Column (DWC): A Dividing Wall Column (DWC) integrates multiple distillation columns into a single shell, allowing concurrent rectification and stripping within separate zones. This configuration enhances thermal coupling, reduces internal reflux requirements, and lowers both energy consumption and capital investment. Simulation and pilot-scale studies by Pedroza et al. (2015) showed that DWC configurations can cut energy usage by up to 40% and produce IAA with purities exceeding 95%, proving their scalability for industrial DWC also reduces the carbon footprint of fusel oil refining, aligning with modern sustainable process design principles (Ferreira & Meirelles, 2013).
- Liquid-Liquid Extraction (LLE): Liquid-liquid extraction exploits the difference in solubility of fusel oil components in two immiscible liquid phases. Solvents such as ethyl acetate, diethyl ether, or water can selectively extract IAA or remove undesired impurities. While the method avoids high-temperature operation, solvent selection and recovery pose major challenges. The solvent must exhibit high distribution coefficients for IAA and low miscibility with water. Furthermore, solvent recycling increases process complexity and cost. Therefore, LLE is typically used as a pretreatment or polishing step rather than the main purification route (Ferreira & Meirelles, 2013).

2.2.2 Feed Purity and Its Effect on Downstream Utilization

The purity of iso-amyl alcohol (IAA) significantly impacts its suitability for chemical synthesis, particularly in esterification to produce iso-amyl acetate (IAAc) and other specialty products. High-purity IAA ($\geq 95\%$) is typically required to achieve efficient reactions, high selectivity, and minimal by-products (Rosa et al., 2014).

Impurities in the IAA feed can have several detrimental effects:

- Formation of undesired esters: Contaminants such as iso-butanol and n-propanol can react with acetic acid to form isobutyl acetate and propyl acetate, reducing the overall yield and selectivity of IAAc (Rosa et al., 2014).
- Catalyst interference: Residual organic acids, sulfur compounds, or esters may alter the activity of catalysts used in esterification. For example, some acidic

impurities enhance catalyst activity transiently but also accelerate deactivation of acid or enzyme catalysts through fouling or poisoning (Santos et al., 2019; Cursaru et al., 2024).

- Water influence on equilibrium: Water, either as an impurity in the feed or as a by-product of esterification, can shift the equilibrium backward according to Le Chatelier's principle, lowering conversion efficiency. Therefore, feed dehydration and water control are critical for maintaining high yields (Wang et al., 2020).
- Product stability and sensory quality: In flavor and fragrance applications, trace levels of low-boiling impurities can alter the aroma profile of iso-amyl acetate, leading to inferior product quality. Hence, purification before esterification not only ensures chemical performance but also sensory consistency.

The control of feed composition thus plays a vital role in downstream processing. Implementing purification strategies—such as final distillation polishing, adsorptive dehydration, or membrane separation—ensures that the IAA feed meets the stringent requirements for both catalytic performance and product quality.

2.3 Reaction Chemistry and Kinetics of Iso-amyl Acetate Synthesis

Esterification Mechanism

The main reaction occurring in the reactive distillation (RD) of iso-amyl acetate is as follows:



This is a reversible reaction, and the conversion is equilibrium-limited. Continuously removing water (e.g., via RD) helps shift the equilibrium toward IAAc formation (Osorio-Viana et al., 2013). The reaction is an acid-catalyzed esterification, where the active site is a proton (H^+), provided by either homogeneous acids (like H_2SO_4) or solid acid catalysts such as Amberlyst or Tulsion resins (Patil & Kulkarni, 2014).

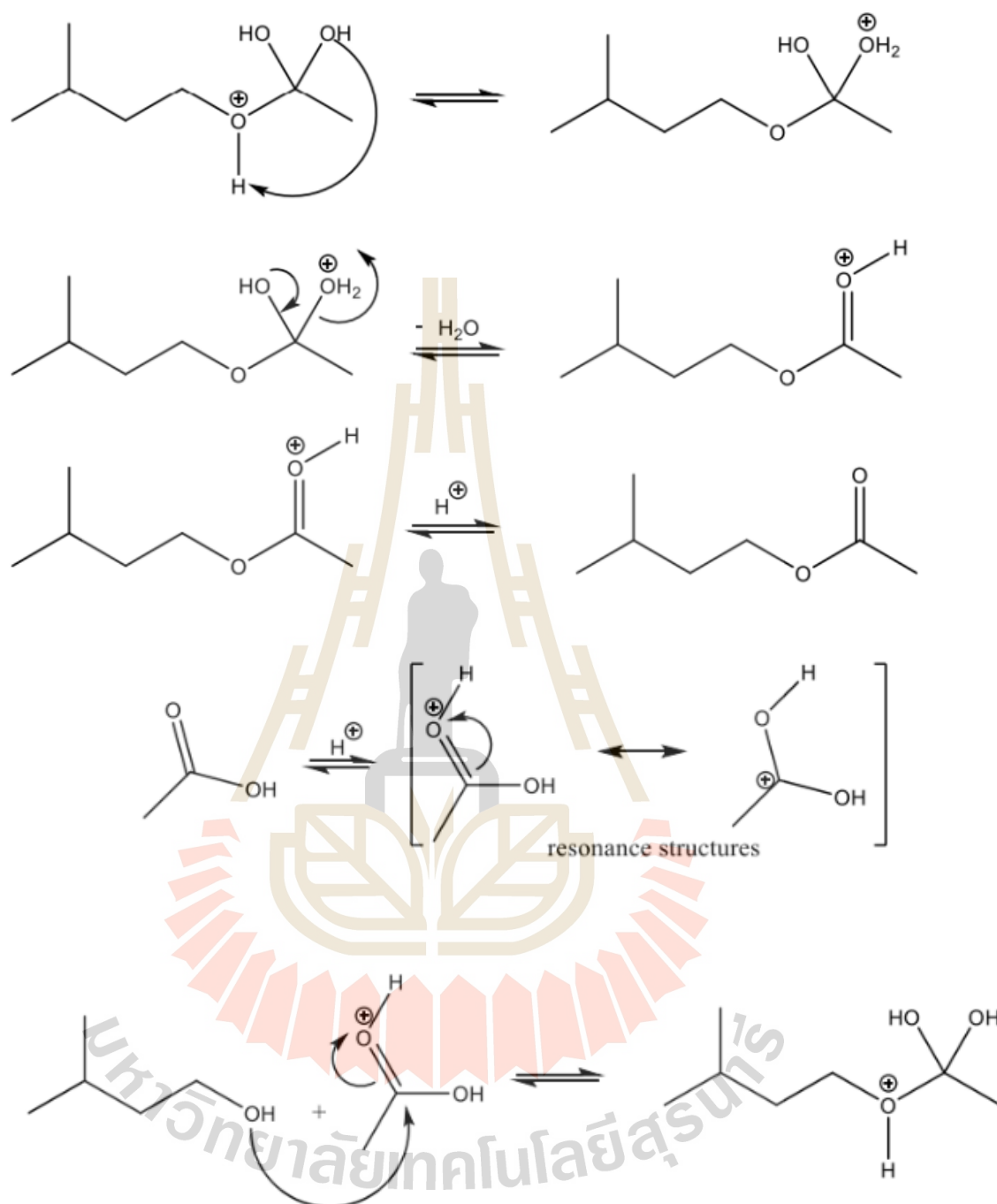


Figure 1. Reaction mechanism of isoamyl acetate synthesis.

2.3.1 Acid-Catalyzed Esterification Mechanism: Iso-Amyl Acetate Synthesis

Iso-amyl acetate (banana oil) is formed by reacting iso-amyl alcohol (3-methyl-1-butanol) with acetic acid under acidic conditions. In this Fischer esterification,

the acid catalyst (H^+) protonates the acetic acid and facilitates a sequence of reversible mechanistic steps (Master Organic Chemistry, n.d.; Westfield State University, n.d.). The mechanism can be divided into six key stages, commonly remembered by the acronym PADPED

- Protonation of the carbonyl oxygen: The reaction begins when the acid catalyst donates H^+ to the carbonyl oxygen of acetic acid, forming a protonated carboxylic acid (oxonium ion). Protonation increases the electrophilicity of the carbonyl carbon, making it more susceptible to nucleophilic attack (Master Organic Chemistry, n.d.; Westfield State University, n.d.). Protonation occurs specifically at the $\text{C}=\text{O}$ oxygen, which is the stronger Lewis base; the positive charge generated is resonance-stabilized across both oxygens (Chemistry Steps, n.d.).
- Nucleophilic addition of iso-amyl alcohol: Iso-amyl alcohol ($\text{R}'\text{OH}$) attacks the proton-activated carbonyl carbon. The lone pair on the alcohol oxygen forms a bond with the carbonyl carbon while the π electrons shift onto the oxygen, generating a tetrahedral intermediate (Master Organic Chemistry, n.d.). Acid catalysis is essential because protonation of the carbonyl greatly enhances its electrophilicity (Westfield State University, n.d.).
- Proton transfers (internal proton shuffle): Proton transfers occur to prepare the leaving group. A base (often water or another alcohol molecule) removes the proton from the $-\text{OHR}'$ group, and the proton is subsequently transferred to the second $-\text{OH}$ group on the tetrahedral intermediate (Master Organic Chemistry, n.d.). This converts a poor leaving group ($-\text{OH}$) into a good leaving group ($-\text{OH}_2^+$), which is necessary for the reaction to proceed (Westfield State University, n.d.).
- Elimination of water: The protonated hydroxyl group leaves as neutral H_2O . As water departs, electrons collapse to reform the carbonyl bond, generating a protonated ester (Master Organic Chemistry, n.d.). This step is only possible because protonation converted $-\text{OH}$ into H_2O , a stable leaving group.

- Deprotonation to form iso-amyl acetate: Finally, a base removes the remaining proton from the protonated ester, regenerating the acid catalyst and
- producing iso-amyl acetate (Master Organic Chemistry, n.d.; Westfield State University, n.d.). The net effect is the replacement of the acetic acid –OH group with the iso-amyl group through acid-mediated proton transfers.

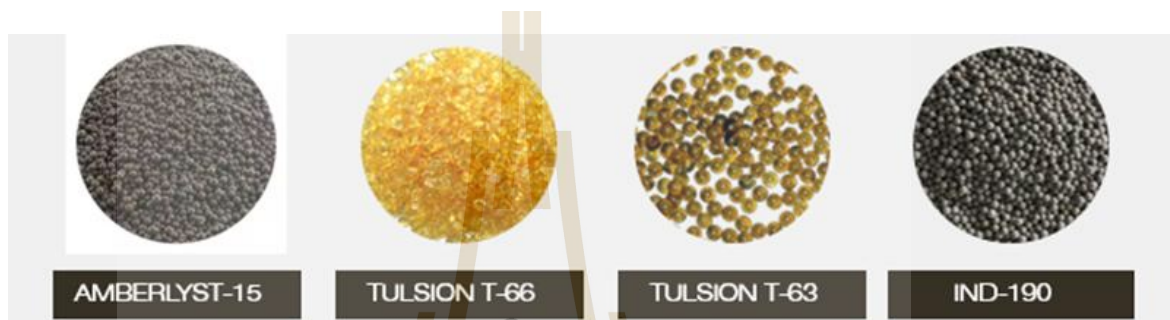


Figure 2. Several heterogeneous resins.

2.4 Catalysts and Kinetics

2.4.1 Homogeneous Acid Catalysts

Homogeneous acids such as sulfuric acid, hydrochloric acid, and p-toluene sulfonic acid have long been employed in esterification because of their strong proton-donating ability and high catalytic activity. Early studies demonstrated that mineral acids dramatically increase reaction rate constants by promoting carbonyl protonation and facilitating nucleophilic attack by alcohols (Patil & Kulkarni, 2014). The mechanism involves protonation of the carbonyl oxygen, formation of a tetrahedral intermediate, and proton-mediated water elimination—steps that are energetically favorable only in the presence of strong acids (Smith & March, 2007). Several authors have reported high conversions of iso-amyl alcohol when homogeneous acids are used, often achieving reaction completion within short residence times under batch conditions (Osorio-Viana et al., 2013). However, these catalysts suffer from inherent limitations: difficulties in separating the acid from the final ester product, corrosion of equipment, and the need for neutralization, which generates substantial wastewater. Additionally, homogeneous catalysts are generally unsuitable for reactive distillation because their volatility or

tendency toward foaming can disturb column hydrodynamics (Sharma & Mahajani, 2003). Consequently, environmental and operational drawbacks have driven research efforts toward greener alternatives.

2.4.2 Heterogeneous (Solid Acid) Catalysts

Solid acid catalysts have emerged as a promising alternative due to their reusability, ease of separation, and compatibility with process intensification strategies. Materials such as Amberlyst-15, Amberlyst-36, Tulsion T-72, and sulfonated. These catalysts operate through fluoropolymer resins (e.g., Nafion) contain immobilized sulfonic acid groups that serve as Brønsted acid sites (Tanabe & Hölderich, 1999)

the same mechanistic pathway as homogeneous acids, although reactions occur at the solid–liquid interface. Protonation of the carbonyl group, nucleophilic addition, and water elimination are facilitated by acidic functional groups located on the polymer matrix (Dias et al., 2013). Numerous studies have demonstrated that Amberlyst-based catalysts provide high ester yields with minimal catalyst leaching (Chakrabarti & Sharma, 1993). Amberlyst-36, in particular, offers improved thermal stability and mechanical strength, making it suitable for high-temperature continuous processes (Mazzocchia et al., 2004). Despite these advantages, heterogeneous catalysts face challenges related to mass-transfer resistance, resin swelling, and long-term deactivation due to fouling or structural degradation. Nevertheless, their operational benefits—including reduced environmental impact and easy recovery—make them ideal for modern esterification systems (Dias et al., 2013). Sulfonated Polymeric Resins as Solid Acid Catalysts for Esterification Sulfonated polymeric resins are among the most established classes of heterogeneous catalysts used in liquid-phase esterification, particularly for the synthesis of medium- to long-chain esters such as iso-amyl acetate. Their strong Brønsted acidity, chemical robustness, and ease of separation make them highly suitable for both batch processes and advanced configurations such as reactive distillation. The most widely studied and industrially utilized resins include Amberlyst-15, Tulsion T-66/T-63, and Indion 190, which share a polystyrene–divinylbenzene (PS–DVB) backbone functionalized with sulfonic acid groups ($-\text{SO}_3\text{H}$), yet differ in porosity, thermal stability, and mass-transfer behavior (Chakrabarti & Sharma, 1993; Tanabe & Hölderich, 1999).

- Amberlyst-15

Amberlyst-15 is considered a benchmark solid acid catalyst for esterification due to its high acidity (4.7–5.0 meq H⁺/g dry), macroreticular porosity, and structural stability (Mazzocchia et al., 2004). The PS–DVB matrix provides a rigid framework that swells moderately in organic systems, enhancing reactant accessibility to internal acid sites. Its strong Brønsted acidity effectively protonates carboxylic acids, thereby accelerating nucleophilic attack by alcohols and promoting formation of the tetrahedral intermediate typical of Fischer esterification. In process intensification technologies such as reactive distillation (RD), Amberlyst-15 serves not only as a catalyst but also as structured packing, enabling simultaneous reaction and separation (Bessling et al., 1997). Despite its strengths, Amberlyst-15 experiences limitations including solvent-induced swelling, susceptibility to fouling by heavy organics, and potential sulfonic acid leaching at temp. The rate of reaction follows a pseudo-homogeneous model, with the rate equation given as:

$$r = k \left(C_{IAA} \times C_{AA} - \frac{C_{IAAc} \times C_{H_2O}}{K_{eq}} \right) \quad (1)$$

Where: r is the reaction rate,

C_{IAA} and C_{AA} are the concentrations of iso-amyl alcohol and acetic acid, respectively,

C_{IAAc} and C_{H_2O} are the concentrations of iso-amyl acetate and water, respectively,

K_{eq} is the equilibrium constant, and

k is the rate constant.

The kinetic parameters for this reaction are:

Rate constant, $k = 2.1 \times 10^{-3} \text{ min}^{-1} = 2.1 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$ at 353 K,

Activation energy, $E_a \approx 45 \text{ kJ/mol}$ (Osorio-Viana et al., 2013; Patil & Kulkarni, 2014). Temperatures above 130–140 °C (Mazzocchia et al., 2004).

- **Tulsion T-66 and T-63**

Tulsion resins, produced by Thermax, have emerged as economically attractive alternatives to Amberlyst catalysts. Tulsion T-66 is a macroreticular strong-acid resin with an acidity comparable to Amberlyst-15 ($\sim 4.8 \text{ meq H}^+/\text{g}$), exhibiting high porosity and rapid reaction kinetics in organic-phase esterification (Thermax, 2018). Its robust structure supports operation in continuous flow and fixed-bed reactors. Tulsion T-63, on the other hand, is a gel-type resin with slightly lower porosity but the same PS-DVB-SO₃H chemical structure. Gel-type resins typically swell more extensively in polar solvents, increasing internal diffusion resistance and potentially reducing catalytic efficiency in bulky alcohol systems such as iso-amyl alcohol (Chakrabarti & Sharma, 1993). Nevertheless, T-63 remains widely used due to its low cost and effective Brønsted acidity in highly polar reaction environments.

The rate equation for this system follows the same kinetic model as Amberlyst but with different kinetic parameters.

The kinetic parameters for this resin are:

T-66: $k = 1.6 \times 10^{-3k} \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$, $E_a \approx 50 \text{ kJ/mol}$,

T-63: $k = 1.4 \times 10^{-3k} \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$, $E_a \approx 52 \text{ kJ/mol}$ (Patil, 2010; Patil & Kulkarni, 2014).

- **Indion 190**

Indion 190 is a macroreticular sulfonated cation-exchange resin with an acid capacity in the range of $4.4\text{--}4.6 \text{ meq H}^+/\text{g}$ and good resistance to organic solvents (Ion Exchange India Ltd., 2015). Its strong acidity and large pore structure make it suitable for esterification and etherification reactions, especially under moderate-temperature liquid-phase conditions. However, the catalyst exhibits slightly lower thermal stability than Amberlyst-36 and experiences higher water retention, which may reduce initial esterification rates due to competitive adsorption at acid sites (Dias et al., 2013). Despite these challenges, Indion 190 remains a cost-effective option for commercial esterification and dehydration applications.

2.5 Reactive Distillation Reactor in Pilot-Plant Scale

The entire unit has a total height of 5.0 meters and was designed and constructed to operate as a continuous system. Purified isoamyl alcohol from the feed tank and acetic acid from the acid feed tank are pumped into the distillation column at the reaction zone. Acetic acid is introduced at the upper part of the reaction zone, whereas isoamyl alcohol, which has a lower boiling point, is fed into the lower part of the reaction zone. The reaction zone consists of a stainless-steel column with a diameter of 3 inches and a length of 1 meter. Within this section, Amberlyst 15E resin (Rohm & Haas, Germany) is used as the solid acid catalyst to supply hydrogen ions (H^+) for the esterification reaction. The catalyst is packed inside metallic structured packing units known as Katapak-SP (Sulzer Chemtech, Switzerland). Ten units of Katapak-SP were installed, resulting in a total catalyst loading of 1 kg. The structured packing is fabricated from stainless-steel mesh sheets folded into multiple layers and tied together, providing internal void spaces for catalyst placement. To promote uniform gas-liquid distribution and minimize pressure drop, the mesh layers are arranged with adequate spacing rather than tightly compacted (Figure 13).

During operation, liquid feeds flow downward while hot vapor rises from the bottom of the column, creating counter-current flow between the vapor and liquid phases. Consequently, fractional distillation is required to separate the ascending vapor stream (in the rectifying section) and the descending liquid stream (in the stripping section). Both the stripping and rectifying sections are constructed from 3-inch glass columns equipped internally with perforated trays. Each tray contains a 10-mm-diameter tube extending 1 cm above the tray surface, functioning as a weir to allow liquid overflow. The lower part of the tube extends approximately 4 cm into the tray below, serving as a downcomer for liquid flow (Figure 14). This tray configuration is particularly suitable for separating liquid mixtures with relatively small differences in boiling points.

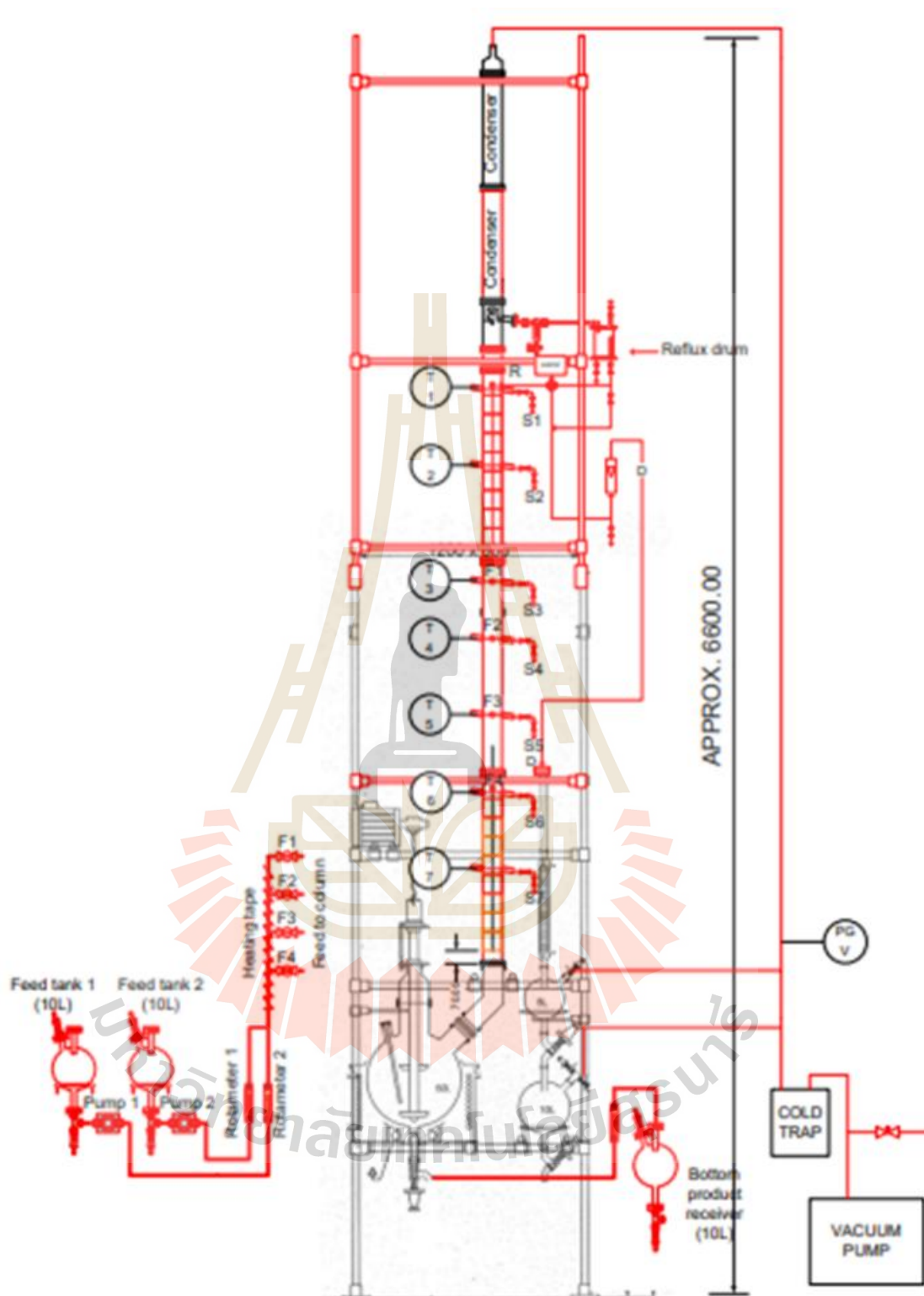


Figure 2. the schematic diagram of the pilot-scale reactive distillation reactor employed in this study.

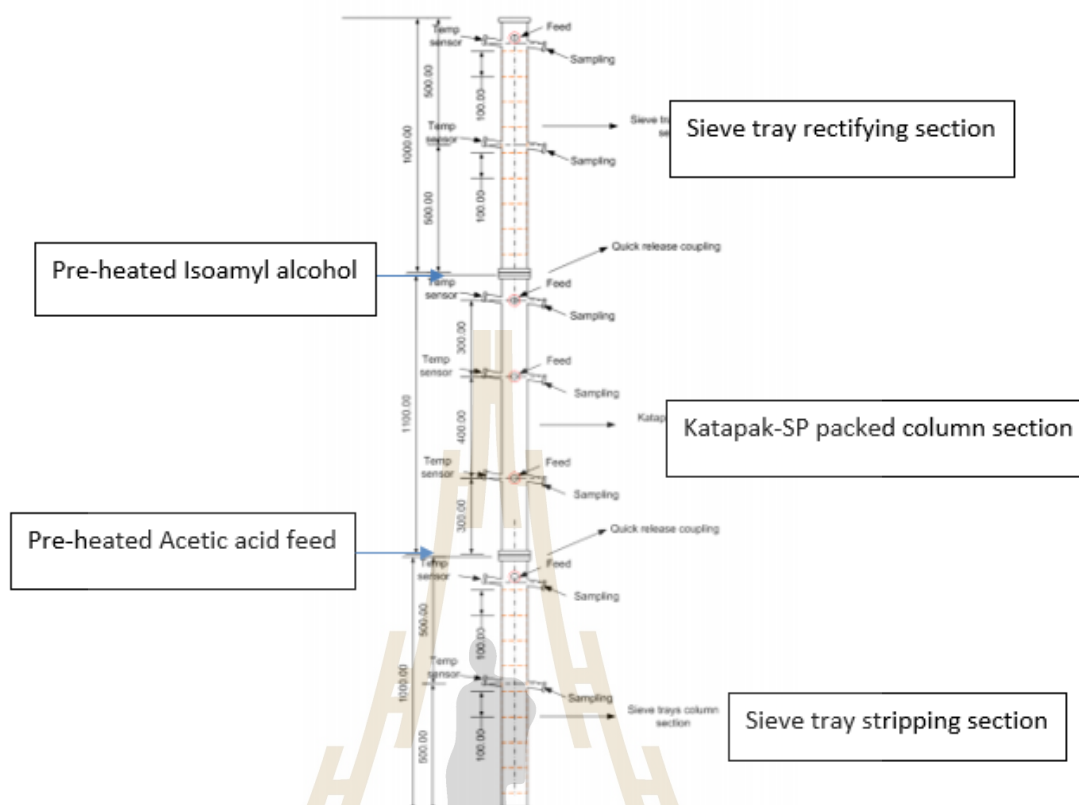


Figure 3. Schematic design of the distillation column trays and the reactive section.

In the rectification section, ten perforated trays are installed. The primary function of this section is to remove light components from the system while returning the heavier, unreacted components back to the reaction zone. Considering the boiling points of acetic acid and isoamyl acetate, both components exhibit significantly higher boiling temperatures than isoamyl alcohol and water. As a result, only water and isoamyl alcohol appear in the overhead vapor. The vapor-liquid equilibrium between water and isoamyl alcohol forms an azeotropic mixture, enabling water to be easily carried upward and condensed. Therefore, increasing the number of trays in this section does not substantially enhance the distillate concentration. The reflux drum subsequently separates the condensed overhead product into two layers, allowing the organic phase (isoamyl alcohol) to be recycled back into the column, while the aqueous phase (water) is removed from the system. For the mixture of isoamyl acetate and isoamyl alcohol in the stripping section, the liquid descending to the bottom of the column ideally contains only these two components, assuming the esterification reaction proceeds to a high conversion. The role of the stripping section is to separate

isoamyl alcohol from isoamyl acetate. Because isoamyl alcohol and isoamyl acetate have significantly different boiling points and do not form an azeotropic mixture, the system can theoretically purify isoamyl acetate to high levels.

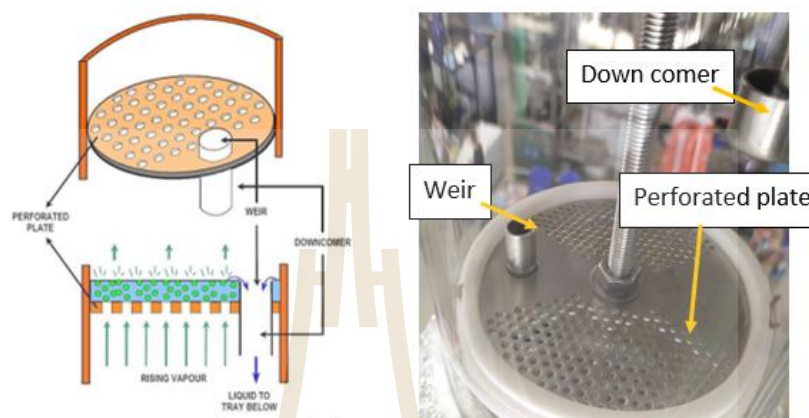


Figure 4. Design of the perforated-plate distillation trays equipped with weirs and downcomers.

This capability directly contributes to enhancing the overall efficiency of isoamyl acetate synthesis. Consequently, the ability of the developed reactive distillation column to achieve both high conversion and high product purity represents a major advantage of the pilot-scale system utilized in this research.

2.6 Working Principle and Simulation of Reactive Distillation (RD) for Isoamyl Acetate Production

2.6.1 Advantages of Reactive Distillation (RD)

The synthesis of isoamyl acetate (IAAc) is conventionally performed through the esterification of isoamyl alcohol (IAA) with acetic acid, an equilibrium-limited reversible reaction. Under standard conditions, the conversion is typically restricted to approximately 70–80% unless the by-product water is removed from the reaction system, as its accumulation shifts the equilibrium back toward the reactants (Patil & Kulkarni, 2014). Reactive distillation (RD) addresses this limitation by integrating the chemical reaction and separation into a single unit. During RD, water—the lightest and most volatile product—is continuously removed from the top of the column, thereby

shifting the equilibrium toward ester formation. As a result, the conversion of IAA can exceed 95% (Lenis, 2014). Beyond the thermodynamic advantages, RD offers several important process benefits:

- Reduction in downstream separation steps: Because reaction and separation occur simultaneously, fewer purification units are required, lowering both capital and energy costs.
- Smaller equipment footprint: The consolidation of reaction and distillation into one apparatus reduces the required plant area.
- Reduced or eliminated solvent usage: Many RD systems avoid the use of entrainers or solvents, thereby minimizing operating costs and environmental impact.
- Simplified scale-up: RD systems are comparatively easier to scale from laboratory to industrial levels due to their compact design and process intensification characteristics (Patil & Kulkarni, 2014; Sánchez et al., 2020).

The kinetic model of the esterification of acetic acid and isoamyl alcohol can be described according to Orjuela (2010), in which the reaction was studied in a batch chemical reactor. The change in the number of moles N_i of component i involved in reaction m can be expressed by Eq. (2):

$$\frac{dN_i}{dt} = N_T \frac{dx_i}{dt} = \left(\sum_{m=1}^M \theta_{i,m} r_m \right) V \quad (2)$$

where N_T is the total number of moles in the reactor, V is the reaction volume, r_m is the reaction rate of reaction m per unit volume, and x_i is the mole fraction of component i in the liquid mixture. The parameter $\theta_{i,m}$ is the stoichiometric coefficient ratio of component i relative to the reference component in reaction m .

Equation (2) can also be expressed in terms of total molar concentration in the liquid phase C_T ($V/N_T=1/C_T$), calculated from the average molecular weight (MW_{Avg}) and solution density:

$$\frac{dx_i}{dt} = \frac{1}{C_T} \left(\sum_{m=1}^M \theta_{i,m} r_m \right) = \frac{MW_{Avg}}{\rho_{Sol}} \left(\sum_{m=1}^M \theta_{i,m} r_m \right) \quad (3)$$

Using the pseudo-homogeneous model for reversible esterification reactions, the reaction rate of acetic acid/isoamyl alcohol esterification can be expressed by Eq. (4):

$$r_1 = w_{CAT} \rho_{Sol} k_0^1 \exp\left(\frac{-E_a^1}{RT}\right) \left[(X_{Acetic\ acid} \gamma_{Acetic\ acid}) (X_{Isoamyl\ alcohol} \gamma_{Isoamyl\ alcohol}) - \frac{(X_{Isoamyl\ acetate} \gamma_{Isoamyl\ acetate}) (X_{H_2O} \gamma_{H_2O})}{K_{Eq}^1} \right] \quad (4)$$

The reacting mixture consists of two reactants (acetic acid and isoamyl alcohol) and two products (water and isoamyl acetate). The non-random two-liquid (NRTL) activity coefficient model was employed to represent vapor–liquid–liquid equilibrium (VLLE) for the quaternary system of acetic acid, isoamyl alcohol, isoamyl acetate, and water (Harmsen et al., 2007). Vapor–liquid equilibrium (VLE) data are available for all binary pairs, and liquid–liquid equilibrium (LLE) data are available for two ternary systems (acetic acid–isoamyl alcohol–water and acetic acid–isoamyl acetate–water) (Chiang et al., 2000).

Table 1. Binary Parameters of the NRTL Model for Acetic Acid (1), Isoamyl Alcohol (2), Isoamyl Acetate (3), and Water (4).

(j, i)	$A_{ij}(K)$	$A_{ji}(K)$	α_{ij}
(1,2)	-316.8	178.3	0.17
(1,3)	-37.94	214.6	0.2
(1,4)	-110.6	424	0.299
(2,3)	-144.8	320.7	0.301
(2,4)	100.1	1448	0.298
(3,4)	254.5	2222	0.2

For reaction-rate calculations, the activity coefficient γ_i is an important thermodynamic parameter. The NRTL activity coefficient model relates γ_i to the mole fraction x_i in the liquid phase and is expressed as:

$$\ln(\gamma_i) = \frac{\sum_{j=1}^n x_j \tau_{ji} G_{ji}}{\sum_{k=1}^n x_k G_{ki}} + \sum_{j=1}^n \frac{x_j G_{ij}}{\sum_{k=1}^n x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_{m=1}^n x_m \tau_{mj} G_{mj}}{\sum_{k=1}^n x_k G_{kj}} \right) \quad (5)$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (6)$$

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} \quad (7)$$

The NRTL model parameters used in this study to describe the quaternary isoamyl acetate esterification system are shown in Tables 3 and 4.

2.6.2 Vapor-Liquid Equilibrium (VLE) and Azeotropes

Vapor-liquid equilibrium (VLE) plays a central role in the design and performance of reactive distillation (RD) for isoamyl acetate production, as it governs both the separation efficiency and the achievable reaction equilibrium. A major challenge arises from azeotropes, which are constant-boiling mixtures that hinder separation. For this reaction system, key azeotropes include:

Table 2. Activity Coefficient Model Parameters for the Isoamyl Acetate Esterification System.

Comp.i	HOAC(1)	HOAC(1)	HOAC(1)	ISAMOH(2)	ISAMOH(2)	ISAMAC(3)
Comp.j	ISAMOH(2)	ISAMAC(3)	H ₂ O(4)	ISAMC(3)	H ₂ O(4)	H ₂ O(4)
B _{ij} (K)	-316.8	-37.943	-110.57	-144.8	100.1	254.47
B _{ji} (K)	178.3	214.55	424.018	320.6521	1447.1	2221.5
C _{ij}	0.1695	0.2	0.2987	0.3009	0.298	0.2

- Water-acetic acid azeotrope: This azeotrope complicates water removal and may allow water to migrate into the bottom product stream if not properly managed.
- Isoamyl alcohol-water azeotrope: Formed at atmospheric pressure, this azeotrope can reduce purity in the overhead and complicate isolation of isoamyl acetate.
- Use of entrainers such as cyclohexane to break azeotropic interactions
- Adjusting column operating pressure to shift azeotrope composition or eliminate azeotropy altogether (Huo et al., 2021)

- To mitigate the limitations imposed by azeotropes, various strategies are commonly employed:

Reliable VLE data is essential for proper RD simulation and design. Such data is typically obtained experimentally and correlated using non-ideal liquid-phase activity coefficient models such as NRTL, UNIQUAC, or, in simpler cases, Wilson (Sutar et al., 2025). The accuracy of these models directly affects predictions of stage requirements, reflux ratio, and overall process efficiency. Incorrect VLE representation can lead to suboptimal design, lower IAAC recovery, reduced conversion, and increased operating costs (Sánchez et al., 2020).

This section presents the thermodynamic analysis of the reaction system for isoamyl acetate synthesis in the reactive distillation (RD) column. Since reactive distillation involves the simultaneous occurrence of esterification and distillation, both the reaction kinetics and the vapor–liquid equilibrium (VLE) must be considered together. VLE describes the relationship between the equilibrium compositions of chemical species in the liquid and vapor phases. According to Raoult's law, the phase-equilibrium relationship can be expressed by Eq. (8):

$$y_i P = x_i \gamma_i P^* \quad (8)$$

where P is the total system pressure; x_i and y_i are the mole fractions of component i in the liquid and vapor phases, respectively; γ_i is the activity coefficient of component i ; and P_i^* is the saturation vapor pressure of pure component i at the given temperature.

The Universal Functional Activity Coefficient model (UNIFAC) is widely used for estimating the activity coefficients of components in non-ideal liquid mixtures. The concept is based on the assumption that molecules are composed of functional groups that interact with other molecules in the mixture. The UNIFAC model consists of two contributions: the combinatorial part (C), which accounts for the entropy effect related to molecular size and shape; and the residual part (R), which represents the enthalpy of mixing and group–group interactions. The activity coefficient can be expressed using Eqs. (9)–(12):

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (9)$$

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i x_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_{j=1}^m x_j l_j \quad (10)$$

$$\ln \gamma_i^R = \sum_{k=1}^m V_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \quad (11)$$

$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1) \quad (12)$$

where z is the coordination number (commonly set to 10); m is the number of components in the mixture; ϕ_i and θ_i are the volume and surface area fractions; and r_i and q_i are the group-based van der Waals volume and surface area parameters, obtained from Eqs. (13)–(16):

$$\phi_i = \frac{x_i r_i}{\sum_{i=1}^m x_i r_i} \quad (13)$$

$$\theta_i = \frac{x_i q_i}{\sum_{i=1}^m x_i q_i} \quad (14)$$

$$r_i = \sum_k V_k^{(i)} R_k \quad (15)$$

$$q_i = \sum_k V_k^{(i)} Q_k \quad (16)$$

where

- $V_k^{(i)}$ is the number of groups of type k in molecule i
- Γ_k is the group activity coefficient in the mixture
- $\Gamma_k^{(i)}$ is the group activity coefficient in pure component i

The group activity coefficient Γ_k is obtained from Eq. (17):

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \theta_m \Psi_{mk} \right) - \sum_m \left(\frac{\theta_m \Psi_{mk}}{\sum_n \theta_n \Psi_{nk}} \right) \right] \quad (17)$$

The group surface area fraction θ_m is calculated using Eq. (18):

$$\theta_m = \frac{Q_m \Psi_m}{\sum_n Q_n \Psi_n} \quad (18)$$

The group mole fraction parameter Ψ_m is defined by Eq. (19):

$$\Psi_m = \exp \left(-\frac{a_{mn}}{T} \right) \quad (19)$$

where a_m the group interaction energy parameter between functional groups m and n

2.7 Aspen Plus Modeling of Reactive Distillation (RD)

Numerous studies have explored the modeling and optimization of reactive distillation systems for isoamyl acetate synthesis using Aspen Plus. A critical aspect of such simulations is the selection of an appropriate thermodynamic property model. The Non-Random Two-Liquid (NRTL) model is most widely applied due to its robustness in representing non-ideal mixtures with strong hydrogen bonding, such as

IAA, acetic acid, and water. In some cases, the UNIQUAC model is used for verification against experimental VLE data, whereas the Wilson model may be used for binary sub-systems (Sánchez et al., 2020; Huo et al., 2021). For RD column simulation, the RadFrac model in Aspen Plus is typically employed. Key design and operating parameters include:

- Number of theoretical stages
- Feed stage locations
- Catalyst distribution within the reactive section
- Reaction kinetics or equilibrium parameters
- Reaction enthalpy and Arrhenius-based rate constants (Lenis, 2014; Sánchez et al., 2020)

Optimization studies have reported significant improvements in both energy usage and economic performance. Rosa et al. (2014) demonstrated that optimizing feed locations and reflux ratios can reduce total energy consumption by approximately 20%. Santos et al. (2019) conducted techno-economic assessments and found that RD processes yield higher Net Present Value (NPV) and Internal Rate of Return (IRR) compared with conventional reactor + distillation sequences. Additionally, Li et al. (2018) proposed a dividing-wall reactive distillation configuration, achieving superior energy efficiency relative to standard RD columns. The reaction kinetics of the esterification process were investigated in this section, and VLE (vapor–liquid equilibrium) data from previously published literature were used to predict the performance of the reactive distillation (RD) column and to validate the developed model. The kinetic expressions and related parameters were applied for the simulation of isoamyl acetate synthesis using the AMBERLYST™ 15 E catalyst.

The reaction rate expression is given by:

$$r = (k_f C_{CH_3COOH} \cdot C_{C_5H_{11}OH} - k_b C_{C_5H_{11}COOCH_3} \cdot C_{H_2O}) \quad (20)$$

Lee et al. (1999) reported a kinetic expression for the synthesis of isoamyl acetate that was used for model development:

$$r = (k_f C_{CH_3COOH} \cdot C_{C_5H_{11}OH} - k_b C_{C_5H_{11}COOCH_3} \cdot C_{H_2O}) \quad (21)$$

$$k_f = 17500e^{-6223.2/T} \quad (22)$$

$$K_{eq} = \frac{k_f}{k_b} = 13.9e^{-777/T} \quad (23)$$

The kinetic parameters are expressed as:

$$K_{eq} = 1.6(T = 363K) \quad (24)$$

The equilibrium constant is defined as: Additional kinetic expressions for the esterification of isoamyl acetate were reported by Patil et al. (2010):

$$k_1 = 3.54 \times 10^3 \exp\left(\frac{-41.88}{RT}\right) \quad (25)$$

where m represents the mass of catalyst (kg). Mass Balance for Reactive Distillation

The mass balance for component i around tray j in the reactive distillation column for isoamyl acetate separation is given by:

$$\frac{d(x_{i,j}M_j)}{dt} = V_j + 1y_{i,j} + 1^{-L_j}x_{i,j+L_j} - 1x_{i,j} - 1^{-V_j}y_{i,j} + \Delta R_{i,j} \quad (26)$$

Expanding the derivative yields:

$$\frac{dx_{i,j}}{dt} + M_j + \frac{dM_j}{dt} x_{i,j} = V_{j+1}y_{i,j+1} - L_jx_{i,j} + L_{j-1}x_{i,j-1} - V_jy_{i,j} + \Delta R_{i,j} \quad (27)$$

The overall mass balance around tray j is:

$$\frac{dM_j}{dt} = V_{j+1} - L_j + L_{j-1} - V_j + \Delta R_j \quad (28)$$

The subscript i ranges from 1 to the number of components, and the subscript j ranges from 1 to the total number of trays (N). Vapor-liquid equilibrium is defined by:

$$y_{i,j} = K_{i,j}x_{i,j} \quad (29)$$

Substituting into the component balance gives:

$$\frac{d(x_{i,j})}{dt} M_j = V_{j+1}K_{i,j+1}x_{i,j+1} - L_jx_{i,j} + L_{j-1}x_{i,j-1} - V_jK_{i,j}x_{i,j} + \Delta R_{i,j} - (V_{j+1} - L_j + L_{j-1} - V_j + \Delta R_j)x_{i,j} \quad (30)$$

Energy Balance for Reactive Distillation

The energy balance around tray j is expressed as:

$$\frac{d(H_{i,j}M_j)}{dt} = V_{j+1}h_{i,j+1} - L_jH_{i,j} + L_{j-1}H_{i,j-1} - V_jh_{i,j} \quad (31)$$

Expanding:

$$\frac{dH_{i,j}}{dt} M_j + \frac{dM_j}{dt} H_{i,j} = V_{j+1}h_{i,j+1} - L_jH_{i,j} + L_{j-1}H_{i,j-1} - V_jh_{i,j} \quad (32)$$

The overall energy balance is:

$$\frac{dH_{i,j}}{dt} M_j = V_{j+1}h_{i,j+1} - L_jH_{i,j} + L_{j-1}H_{i,j-1} - V_jh_{i,j} - (V_{j+1} - L_j + L_{j-1} - V_j + \Delta R_j) + H_{i,j} \quad (33)$$

These governing equations are solved simultaneously with the algebraic equations describing the reaction kinetics and vapor–liquid equilibrium (VLE), enabling accurate simulation of the reactive distillation process for isoamyl acetate production.

2.8 Analysis Chemicals and Standards

Acetic acid (99.8%), isoamyl alcohol (99%), and isoamyl acetate (>99% purity) were purchased from Merck® and used as analytical standards. Analysis of Volatile Compounds: Volatile compounds such as isoamyl acetate and isoamyl alcohol in ester form were quantified using a gas chromatograph (GC) equipped with a flame ionization detector (FID) (Agilent, USA). Helium (99.99%) was used as the carrier gas. The GC column employed was a Carbowax column (Restek, USA) with dimensions 30 m × 0.32 mm, bonded-phase fused silica capillary. Operational parameters were as follows:

- Injector temperature: 250°C
- Detector temperature: 300°C
- Oven temperature program: 50–250°C with a heating rate of 15°C/min
- Injection volume: 0.5 μL



Figure 5. Gas Chromatograph–FID (left) and Karl Fischer Titration Setup.

Physical and Chemical Property Analysis of Isoamyl Acetate

The physical and chemical characteristics of isoamyl acetate were examined, including: The analysis of the above parameters ensures accurate and reliable results, which can then be used for benchmarking and further development toward commercial-scale

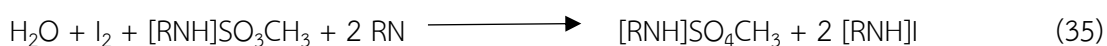
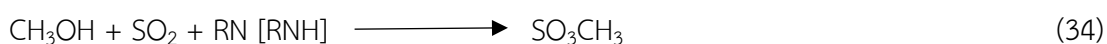
production. The moisture content in the samples was analyzed using the HYDRANAL® – Moisture Test Kit (Sigma-Aldrich). The principle of this method is based on the oxidation reaction of sulfur dioxide by iodine (Hydranal®) in the presence of water in the sample. This reaction is highly suitable for determining trace amounts of water contamination in samples. In the HYDRANAL® – Moisture Test Kit, the procedure begins by adding HYDRANAL®-Solvent E into the titration vessel.

Any pre-existing water in the vessel is first removed by titrating with HYDRANAL®-Titrant Component until the endpoint is reached, which is indicated by a color change from clear to yellow.

Table 3. Linear Regression Analysis of Calibration Curves of Various Standard Compounds Analyzed by Gas Chromatography.

component	Retention time (min)	Range (ppm)	Equation	R ²
Ethanol	4.9	10-500	$Y = 0.0001(x) - 0.0033$	1.0
Propanol	9.7	10-500	$Y = 0.0013(x) + 0.05$	1.0
1-Butanol	13.1	10-500	$Y = 0.0038(x) + 0.0184$	0.9986
Iso-butanol	11.9	10-500	$Y = 0.0037(x) + 0.0728$	0.9997
Isoamyl-alcohol	15.2	10-500	$Y = 0.0094(x) + 0.0607$	0.9982

For each sample analysis, a syringe is used to withdraw the required volume of the sample for moisture determination. The sample is then titrated again with HYDRANAL®, following the Karl Fischer reaction, represented by the following equations:



In this reaction, water and iodine react in a 1:1 molar ratio. Karl Fischer titration is considered the most accurate method for measuring trace water content in ethanol and other organic solvents in which water is partially soluble. Before determining the moisture content of the sample, the titre value (b) [mg water/mL] must be established. This is done by titrating HYDRANAL®-Standard, which contains 5 mg of water per mL. A 0.50 mL aliquot of the standard is titrated with HYDRANAL®-Titrant Component until the endpoint.

The titre (b) is calculated using:

$$b = (5.0 * 0.50)/a \quad (36)$$

where:

a = volume of HYDRANAL®-Titrant Component used (mL)

The percentage moisture content in the sample (ccc), expressed as percent by volume, is calculated using:

$$c = a * b * 100 / V \quad (37)$$

where:

- a = volume of HYDRANAL®-Titrant Component used (mL)
- b = titre value obtained from Equation (36)
- V = volume of the sample (μL)

Note: At 20°C, the density of ethanol is 0.7893 g/mL, and the density of water is 0.9982 g/mL.

CHAPTER III

RESEARCH METHODOLOGY

3.1 Feedstock Preparation and Characterization

The fusel oil used as feedstock is sourced from Katis Bioethanol Co., Ltd. The composition of fusel oil is analyzed, focusing on the identification and quantification of higher alcohols, particularly isoamyl alcohol (IAA), using Gas Chromatography- Flame Ionization Detector (GC-FID) techniques.

Table 5. the analytical results of the fusel oil obtained from Katis Bioethanol Co., Ltd.

Test item	Test Method	Unit	Value
H2O	Karl's Fischer	%wt	17.5
Alcohols	GC-FID		
Ethanol		%wt	6.85
Propanol		%wt	9.43
1-Butanol		%wt	0.61
iso-Butanol		%wt	10.52
iso-amyl alcohol		%wt	55.1
Metals	ICP-OES		
Arsenic		mg/kg	< 0.1
Mercury	Mercury analyzer	mg/kg	< 0.01
Flash point	ASTM D 93-20	°C	37

3.2 Separation and Purification of Isoamyl Alcohol (IAA)

The separation and purification of isoamyl alcohol (IAA) were performed through fractional distillation at the Pilot Plant, Suranaree University of Technology (SUT).

This process was selected due to its capability to effectively separate components with close boiling points and to obtain high-purity IAA from the fusel oil feedstock. The distillation system consisted of a stainless-steel column equipped with a reflux condenser, reboiler, temperature controllers, and sampling ports. The operation was carried out under atmospheric pressure, with column temperatures maintained in the range of 120–140 °C, depending on the composition of the feed. The reflux ratio and heating rate were optimized to achieve efficient vapor–liquid equilibrium and enhance the recovery of isoamyl alcohol, whose normal boiling point is approximately 131 °C.



Figure 1. Fusel oil obtained from Katis Bioethanol Co., Ltd.

The operation was carried out under atmospheric pressure, with column temperatures maintained in the range of 120–140 °C, depending on the composition of the feed. The reflux ratio and heating rate were optimized to achieve efficient vapor–liquid equilibrium and enhance the recovery of isoamyl alcohol, whose normal boiling point is approximately 131 °C. The obtained distillate fractions were analyzed to determine purity and composition using Gas Chromatography–FID. The purity of IAA and the energy consumption of the distillation process were further compared with simulation results obtained from Aspen Plus. The fractional distillation in this section is

carried out under controlled conditions using a pilot-scale distillation column that was designed and constructed in-house at Suranaree University of Technology, as shown in Figure 8 (bottom). The separation principle relies on differences in the boiling points of the components. By applying heat to the mixture, each component vaporizes at its characteristic vapor pressure, allowing separation based on boiling-point differences. The main heating system consists of a 100-liter reactor equipped with a double-layered vessel that allows thermal oil to circulate through the outer jacket. Three electric heating rods, each rated at 6 kW, provide the heat. The top of the reactor is connected to a custom-designed sieve-tray (perforated plate) distillation column. The complete pilot-scale system has a total height of 5.0 meters. The column operates continuously. Fusel oil is pumped through a pre-heater before entering the column at the feed stage located at the mid-section. The column is constructed from a stainless-steel cylinder with a 5-inch diameter and a height of 4.5 meters. Internally, the column contains flat perforated trays. Each tray is fitted with a 1-inch diameter pipe whose upper end extends 1 cm above the tray surface, acting as a weir for liquid overflow. The lower end of the pipe protrudes 4 cm below the tray, functioning as a downcomer, as illustrated in Figure 8 (top). Fractional distillation is suitable for mixtures with components that have relatively small differences in boiling point. During operation, rising vapor passes through the perforations on the trays. A portion of the vapor condenses on each tray, increasing the liquid holdup until it overflows the weir and flows downward through the downcomer. This simultaneous vapor-liquid contacting across multiple trays is equivalent to performing numerous simple distillations at once. Both the stripping and rectifying sections of the column contain 15 trays each. The feed (fusel oil) is introduced after being heated in a pre-heater. At the top of the column, a condenser is installed to convert vapor into liquid using cooling water as the heat-exchange medium. The condensed liquid flows into a reflux drum. The reflux system in this work is specially designed to allow direct control of the reflux ratio in the column, enabling efficient regulation of the isoamyl alcohol concentration obtained from the distillation. Heat is supplied from the reboiler via thermal oil pumped into the jacket of the reactor. To obtain comprehensive data for this research, operating variables such as feed flow rate and reboiler temperature will be investigated to determine the optimal conditions for distilling isoamyl alcohol with high yield and

efficiency, the heat-exchange medium. The condensed liquid flows into a reflux drum. The reflux system in this work is specially designed to allow direct control of the reflux ratio in the column, enabling efficient regulation of the isoamyl alcohol concentration obtained from the distillation. Heat is supplied from the reboiler via thermal oil pumped into the jacket of the reactor. To obtain comprehensive data for this research, operating variables such as feed flow rate and reboiler temperature will be investigated to determine the optimal conditions for distilling isoamyl alcohol with high yield and efficiency. concentration obtained from the distillation. Heat is supplied from the reboiler via thermal oil pumped into the jacket of the reactor. To obtain comprehensive data for this research, operating variables such as feed flow rate and reboiler temperature will be investigated to determine the optimal conditions for distilling isoamyl alcohol with high yield and efficiency.

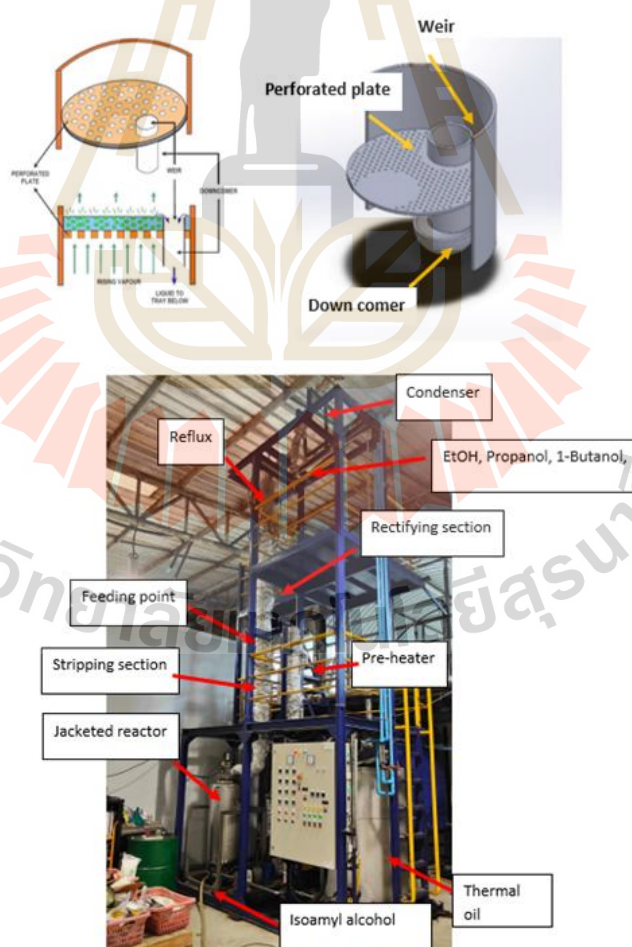


Figure 2. fractional distillation at the Pilot Plant, Suranaree University of Technology.

3.3 Esterification Kinetics Study

The esterification reaction for synthesizing isoamyl acetate is studied:

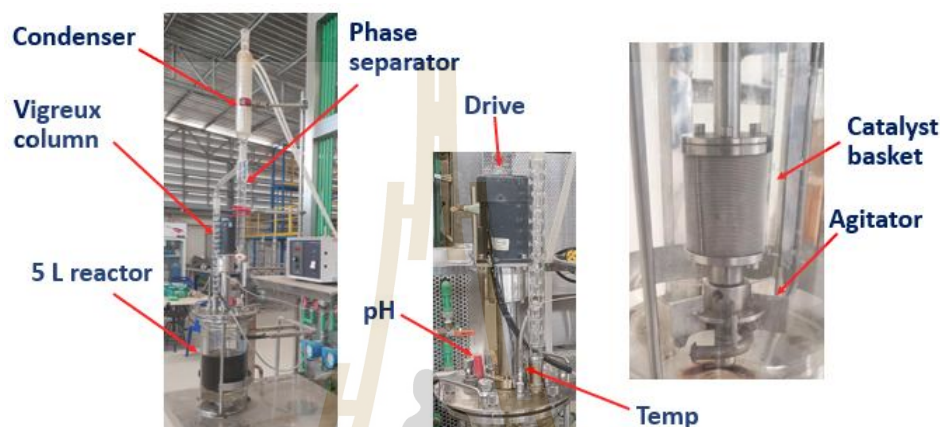
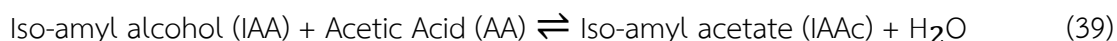


Figure 3. pilot-scale reaction apparatus.

In this study, various catalysts were evaluated for their performance in promoting the reaction, including Amberlyst-15, Tulsion T-66/T-63, and IND-190 for comparison purposes. The main objective was to determine the rate constants (k), activation energy (E_a), and equilibrium constant (K_{eq}) based on data obtained from batch reactor experiments and supporting literature sources (Tiwari & Mahajani, 2015; Patil & Kulkarni, 2014). Catalyst screening and parameter studies were conducted in a 5 L three-neck round-bottom batch reactor equipped with a reflux condenser, thermometer, and magnetic stirrer. The reaction mixture consisted of isoamyl alcohol and acetic acid at molar ratios ranging from 1:1 to 1:5, with Amberlyst-15E catalyst loaded at 5–15 wt% relative to the amount of alcohol. The reaction was carried out under atmospheric pressure, with temperatures between 60 and 100 °C and continuous agitation to ensure homogeneity. Samples were withdrawn periodically and analyzed using Gas Chromatography (GC-FID, Agilent 6890) to determine isoamyl acetate concentration and conversion, while the water content was measured by Karl Fischer titration.

Batch Experiments

- Reactor Setup: A 5 L three-neck round-bottom batch reactor, equipped with a magnetic stirrer, reflux condenser, and thermometer, was used.
- Initial Charge: A fixed molar ratio of Iso-amyl alcohol (IAA) Acetic Acid(AA) (1:3) and a fixed catalyst loading (15wt % relative to the alcohol) were charged into the reactor.
- Heating and Agitation: The reaction mixture was heated to a specified temperature under continuous agitation (200 rpm) at atmospheric pressure.
- Catalyst Evaluation: Separate batch runs were conducted using each of the candidate catalysts: Amberlyst-15, Tulsion T-66, Tulsion T-63, and IND-190.
- Sampling: Liquid samples (0.5 mL) were withdrawn periodically (every 10 minutes) over a defined reaction time (6 hours).
- Analysis: The concentration of IAAC and AA in each sample was determined using Gas Chromatography (GC-FID) to calculate the conversion efficiency and reaction rate for each catalyst.
- Selection: The catalyst demonstrating the highest conversion efficiency (typically Amberlyst-15) was selected for the subsequent sensitivity analysis and kinetic study. Sensitivity Analysis and Optimization: The selected catalyst, typically Amberlyst-15, was employed to investigate the effects of key operating parameters on the esterification performance. The following factors were systematically varied:
 - Effect of Temperature: The experiments were conducted at a fixed catalyst loading and molar ratio, while the reaction temperature was varied from 60 to 100 °C. The reaction was conducted using AMBERLYST™ 15E at a catalyst loading of 15 wt%, an agitation speed of 200 rpm, and a molar ratio of isoamyl alcohol to acetic acid of 1:3. The influence of temperature on conversion and rate was analyzed, and the activation energy (E_a) was determined from the temperature dependence of the rate constant.

- Effect of Catalyst Loading: At the optimal reaction temperature and fixed molar ratio, the catalyst loading (based on the mass of isoamyl alcohol, IAA) was varied between 5–15 wt%. The reaction was conducted at 70 °C with a molar ratio of isoamyl alcohol to acetic acid of 1:3, under an agitation speed of 200 rpm. The objective was to evaluate how catalyst quantity affects the reaction rate, equilibrium conversion, and product yield.
- Effect of Molar Ratio (IAA : Acetic Acid): The molar ratio of isoamyl alcohol to acetic acid (IAA:AA) was varied from 1:1 to 1:3 under optimal temperature and catalyst loading conditions. AMBERLYST™ 15E was employed at a catalyst loading of 5 wt% under reaction conditions of 70 °C and an agitation speed of 200 rpm. This analysis assessed the influence of excess acetic acid on the equilibrium conversion and purity of isoamyl acetate (IAAc).

3.4 Aspen Plus Simulation of RD Process

The Reactive Distillation (RD) simulation was performed using Aspen Plus V14.0 with the objective of determining the optimal operating conditions including reflux ratio, column temperature profile, and feed flow rate for the pilot-scale RD column at the SUT Pilot Plant. The simulation aimed to achieve the maximum conversion of reactants and the highest purity of isoamyl acetate (IAAc) in the Bottom product.

The model configuration was based on the actual pilot column, consisting of 30 theoretical stages with 10–15 reactive stages located in the middle section. The acetic acid (AA) feed was introduced at stage 10, while the isoamyl alcohol (IAA) feed was introduced at stage 15. The NRTL property method was selected for representing the thermodynamic behavior of the non-ideal system, and the UNIQUAC model was used for cross-validation. Experimental data from Section 5.1 (Feedstock Preparation and Characterization) were used to define the feed composition and molar ratio of IAA to AA, while reaction kinetics were adopted from laboratory-scale studies. A sensitivity analysis was performed by varying key parameters such as reflux ratio and feed flow

rate to identify the optimal operating window that maximized isoamyl acetate yield, conversion, and product purity, while minimizing energy consumption. Pilot-scale experimental runs were conducted using the operating parameters obtained from the Aspen Plus simulation to validate the process performance of the reactive distillation (RD) system. The experiments aimed to confirm the predicted results in terms of isoamyl alcohol (IAA) conversion and isoamyl acetate (IAAc) product purity. The RD column was operated under controlled conditions at the SUT Pilot Plant, following the optimal reflux ratio, feed flow rate, and temperature profile identified through simulation. The collected samples from the distillate and bottom streams were analyzed using Gas Chromatography (GC-FID) for composition and Karl Fischer titration for water content determination. The experimental data were compared with simulation outputs to assess model reliability and scalability from laboratory to pilot level.

3.5 Pilot Scale experimental

Pilot-scale experimental runs were conducted using the operating parameters obtained from the Aspen Plus simulation to validate the process performance of the reactive distillation (RD) system. The experiments aimed to confirm the predicted results in terms of isoamyl alcohol (IAA) conversion and isoamyl acetate (IAAc) product purity. The RD column was operated under controlled conditions at the SUT Pilot Plant, following the optimal reflux ratio, feed flow rate, and temperature profile identified through simulation. The collected samples from the distillate and bottom streams were analyzed using Gas Chromatography (GC-FID) for composition and Karl Fischer titration for water content determination. The experimental data were compared with simulation outputs to assess model reliability and scalability from laboratory to pilot level.

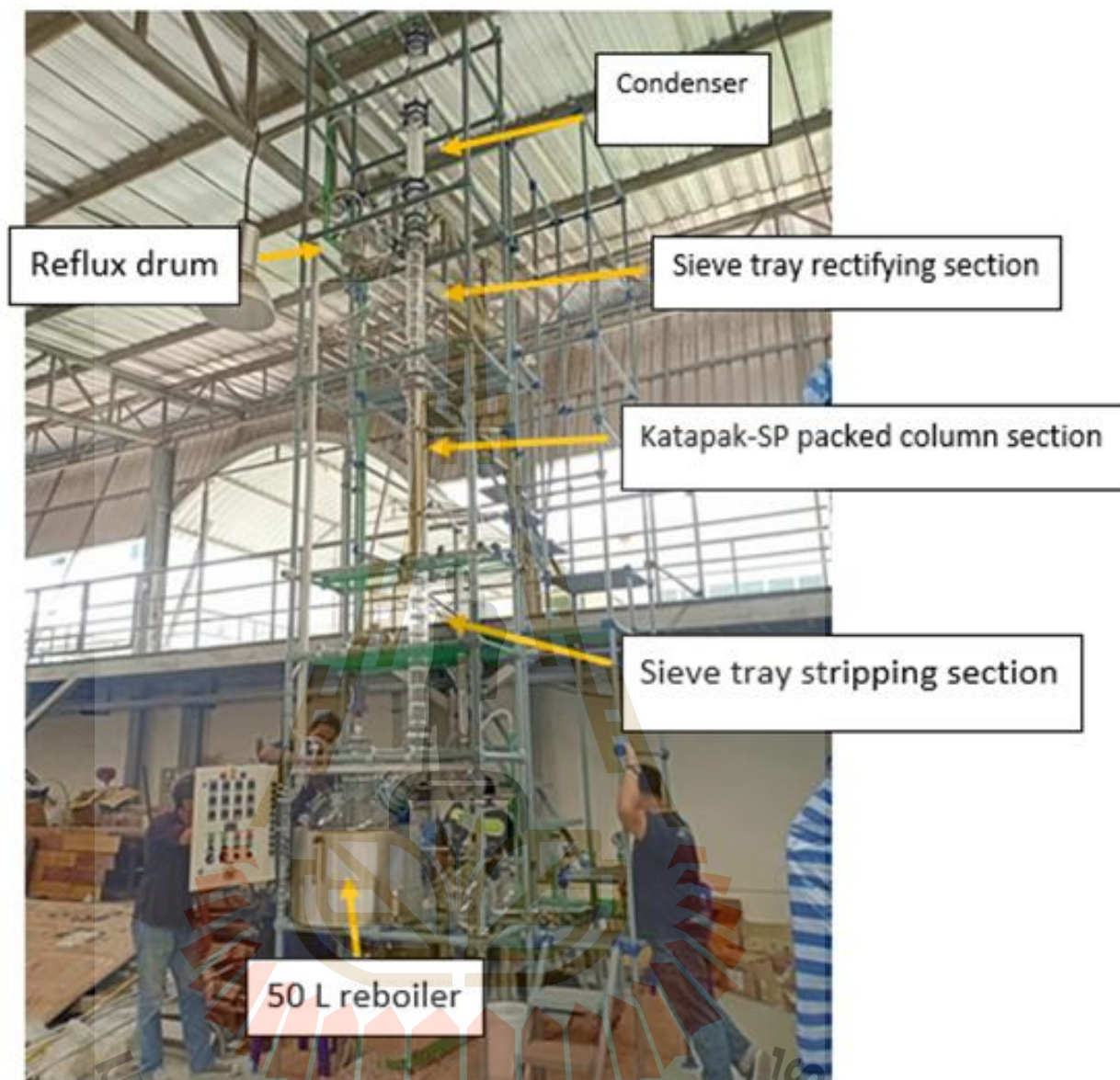


Figure 4. Pilot-scale 50-L reactive distillation column for isoamyl acetate production.

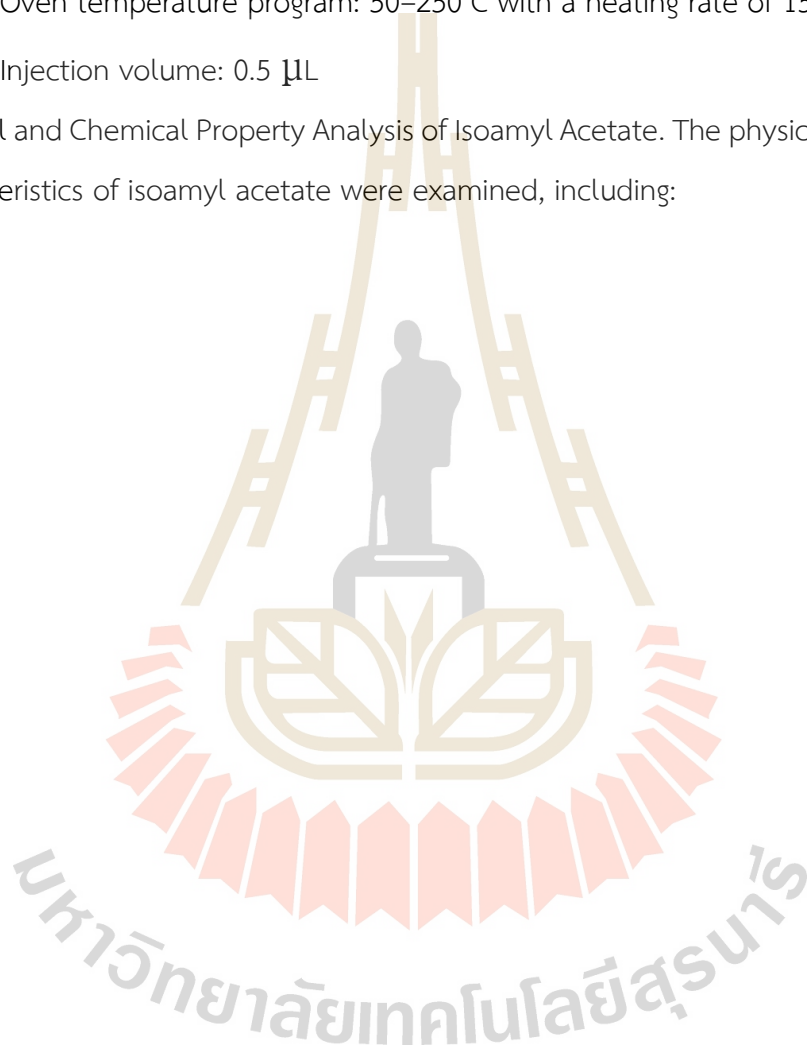
3.6 Analysis Chemicals and Standards

Acetic acid (99.8%), isoamyl alcohol (99%), and isoamyl acetate (>99% purity) were purchased from Merck® and used as analytical standards. Analysis of Volatile Compounds Volatile compounds such as isoamyl acetate and isoamyl alcohol in ester form were quantified using a gas chromatograph (GC) equipped with a flame ionization detector (FID) (Agilent, USA). Helium (99.99%) was used as the carrier gas.

The GC column employed was a Carbowax column (Restek, USA) with dimensions 30 m × 0.32 mm, bonded-phase fused silica capillary. Operational parameters were as follows:

- Injector temperature: 250°C
- Detector temperature: 300°C
- Oven temperature program: 50–250°C with a heating rate of 15°C/min
- Injection volume: 0.5 μL

Physical and Chemical Property Analysis of Isoamyl Acetate. The physical and chemical characteristics of isoamyl acetate were examined, including:



CHAPTER IV

RESULT AND DISCUSSION

4.1 Fractional Distillation of Industrial Fusel Oil for the Production of Isoamyl Alcohol

In this section, the fractional distillation process was operated under controlled conditions using a pilot-scale distillation unit designed and constructed in-house at Suranaree University of Technology (Figure 8). The system functions based on the principle of separating liquid components according to differences in their boiling points. Upon heating, each component vaporizes at its characteristic vapor pressure, enabling phase separation. The main heating system consists of a 100-liter double-jacket reactor, where thermal oil circulates through the outer jacket. Three heating rods, each with a capacity of 6 kW, provide the required heat. The reactor is connected to a pilot-scale sieve-tray (perforated plate) distillation column with a total height of 5.0 meters. The column is constructed from stainless steel, with a diameter of 5 inches and an internal column height of 4.5 meters.

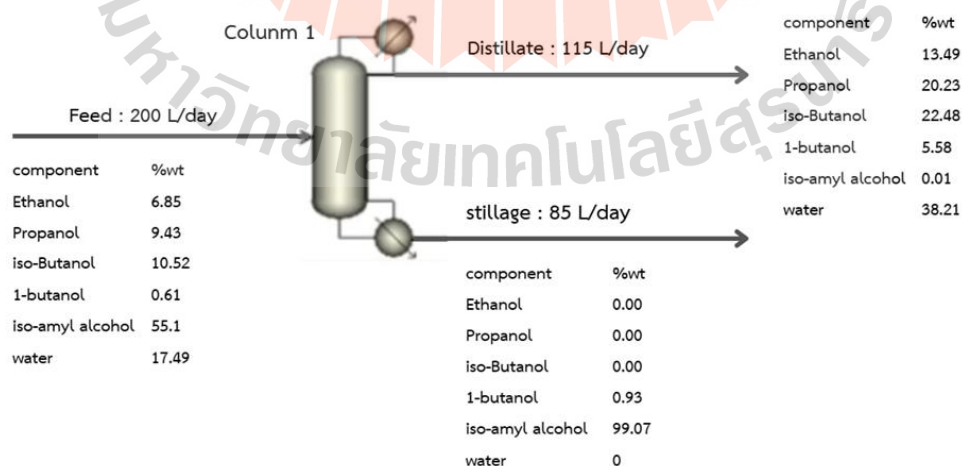


Figure 11. Mathematical simulation-based design of the fusel oil distillation system.

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TEST REPORT

Customer : KTIS BioEthanol Company Limited,
24 Aekphol Bldg., Vibhavadi Rangsit Rd.,
Dinsoeng, Bangkok 10400 Thailand
Tel : 02-692-0859-66, 081-258-5762
Fax : 02-246-9125
Email : goong_goong12@hotmail.com
Contact person : K. Panadda S.

Test report no. : MTP/2025/02363
Revision no. : 0
Report date : 08-04-2025
Sample received date : 01-04-2025
Sample tested date : 02-04-2025
Test completed date : 07-04-2025

Sample description
Sample no. : MTP/2025/02363-01
Sample submitted by : Customer
Sample condition : Colorless liquid

Customer Information
Sample name : Alcohol (Iso amyl alcohol)

Test Parameter	Test Method	Unit	Results
Appearance	Visual	-	Colorless liquid
IR Spectrum	FTIR Spectrum	-	See the attached
Refractive Index at 20 deg. C	ASTM D1218-21	-	1.4065
Purity	GC-FID	%wt	99.61
Solubility	BP 2019	-	-
- Turbidity (1ml/3ml 60% Ethanol)		-	Clear
- Color		-	Colorless
Acidity as Acetic Acid	BP 2019	mg/L	28
Specific Gravity at 20/4 deg. C	ASTM D4052-22	-	0.8063
Heavy metals			
- Pb	ICP-OES	mg/kg	Less than 1
- As	ICP-OES	mg/kg	Less than 1
- Cd	ICP-OES	mg/kg	Less than 1
- Hg	CV-AAS	mg/kg	Less than 0.1
Proton NMR Spectrum ^(Note)	NMR Spectrum	-	See the attached

Note : These test was subcontracted to external laboratory.

Remark : "The test results relate only to the items tested and are not intended to be a recommendation for any particular course of action. Customer is responsible for acting as it sees fit on the basis of such results. All work is performed in accordance with Intertek Standard Terms And Conditions of Service which is Available on request and at <http://www.intertek.com/terms>. This report (including any enclosures and attachments) has been prepared for the exclusive use and benefit of the addressee(s) and solely for The purpose for which it is provided. Unless we provide express prior written consent, no part of this report should be reproduced, distributed or communicated to any third part. We do not accept any liability if this report is used for an alternative purpose from which it is intended, nor do we owe any duty of care to any third part in respect of this report. Tests marked (*) are not under scope of accreditation."

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Approved by  Sam Jirunwanich
Laboratory Manager

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Map Ta Phut Laboratory : 22 Noen Sami Road, Noen Phra Subdistrict, Mueang Rayong District, Rayong Province 21150, Thailand. Tel: +66 2765 2999, +66 8 1359 6754



Figure 12. Physical and chemical property analysis.

Table 6. Chemical composition analysis of fusel oil obtained from the factory (feedstock) and after fractional distillation.

Test item	Feed (%wt)	Distillate (%wt)	Stillage(%wt)	BP (°C)
Alcohols				
- Ethanol	6.85	13.49	0.00	78
- Propanol	9.43	20.23	0.00	97
- iso-Butanol	10.52	22.48	0.00	108
- 1-Butanol	0.61	5.58	0.93	117.7
- iso-amyl alcohol	55.1	0.01	99.07	130
H ₂ O	17.49	38.21	0.00	100
total (%)	100	100	100	
Volume (L)	200	115	85	



Figure 13. samples of the Bottom product, isoamyl alcohol and heavy bottom impurity.

The feed, fusel oil, is pumped through a pre-heater before entering the column at the mid-section. Inside the column, flat perforated trays are installed, each equipped with a 1-inch downcomer. The upper section of the downcomer protrudes

1 cm above the tray surface, functioning as a weir to regulate liquid holdup on each tray. The lower end of the downcomer extends approximately 4 cm below the tray to allow liquid to flow steadily to the tray below. Fractional distillation is particularly suitable for separating liquid mixtures with closely spaced boiling points.

During distillation, vapor rises through the perforations in each tray (rising vapor), while part of the vapor condenses, increasing the liquid level until it overflows the weir and moves to the lower tray. This counter-current contact results in repeated condensation–vaporization cycles, effectively performing many simple distillation steps simultaneously. Both the rectifying and stripping sections of the column consist of 15 trays each.

The fusel oil feed is pumped into the column through a heat exchanger (pre-heater) to raise its temperature. At the top of the column, a condenser is installed to liquefy the overhead vapor using cooling water as the heat-exchange medium. The condensed liquid flows into a reflux drum specially designed to directly control the reflux ratio, enabling precise adjustment of the isoamyl alcohol concentration in the distillate. The system is heated through the thermal-oil circulation in the reactor's outer jacket. To obtain complete operational data, this research investigates variables such as feed rate and reboiler temperature to optimize isoamyl alcohol separation, ensuring high yield and process efficiency. The distillate, consisting mainly of ethanol, propanol, and 1-butanol, can be dehydrated and blended into fuel-grade ethanol or used as a component in various gasohol formulations. To determine the optimal continuous distillation conditions, fusel oil was fed at the mid-section of the column at a rate of 50 liters per hour. The thermal oil temperature was adjusted such that the temperature of the heavy liquid (stillage) ranged from 120 °C to approximately 128 °C, which is close to the boiling point of isoamyl alcohol (130 °C). During these tests, both the distillate and bottoms were recycled back into the system, a procedure known as total recycle mode, until steady-state conditions were achieved. After reaching the optimal conditions, the product streams were separated for further processing. Collected samples from both the distillate and the bottoms were analyzed for chemical composition using gas chromatography equipped with a Flame Ionization

Detector (GC-FID). The water content in the samples was determined using Karl Fischer titration. The fractional distillation of 200 liters of fusel oil obtained from an ethanol production facility was conducted using a continuous pilot-scale distillation column. The feed rate was maintained at $50 \text{ L}\cdot\text{h}^{-1}$, and experimental results revealed that the optimal operating condition was achieved when the temperature of the bottom liquid was controlled at 128°C , a value close to the boiling point of isoamyl alcohol (130°C). Under these conditions, the bottom product reached an isoamyl alcohol purity of 99.07%, with only 0.93% butanol remaining as a minor impurity. The loss of isoamyl alcohol to the overhead stream was minimal, amounting to only 0.01% of the total product, confirming the high separation efficiency of the system. Despite the high purity, the purified isoamyl alcohol developed a yellow coloration when stored in clear glass containers exposed to light. This behavior is consistent with photo-degradation processes, as reported in the literature, and it is therefore recommended that the product be stored in amber or opaque bottles to minimize light-induced degradation. The overhead distillate was composed of ethanol, propanol, isobutanol, butanol, and water in proportions of 13.49%, 20.23%, 22.48%, 5.58%, and 38.21%, respectively. Although the overhead distillate appeared clear, the bottom stream exiting the column displayed a dark brown color, indicating the presence of heavier organic impurities. To achieve the desired purity, the bottom product was subjected to further purification using a 20-liter vacuum rotary evaporator. This additional step successfully yielded a clear and highly purified isoamyl alcohol, which was subsequently used in the reactive distillation experiments for isoamyl acetate synthesis. In total, 80 liters of high-purity isoamyl alcohol were produced. As the composition of fusel oil varies depending on fermentation conditions, raw material from each batch must be analyzed prior to processing. Although the variation may affect the total amount of alcohol recovered, the fractional distillation system consistently provided high-purity isoamyl alcohol regardless of feed variability. A production capacity assessment was conducted based on the continuous distillation of fusel oil at a feed rate of $50 \text{ L}\cdot\text{h}^{-1}$, corresponding to $400 \text{ L}\cdot\text{day}^{-1}$ for an 8-hour

operating period. At this rate, and with an isoamyl alcohol content of 55.1% in the raw fusel oil, the daily recovery of purified isoamyl alcohol was calculated as $218.4 \text{ kg}\cdot\text{day}^{-1}$, assuming 99.07% purity and no residual water. This value significantly surpasses the initial design target, which aimed for the processing of 100 L of fusel oil per day to obtain at least $50 \text{ kg}\cdot\text{day}^{-1}$ of isoamyl alcohol at a purity greater than 99%.

From the production perspective, processing 100 L of fusel oil per day containing 55.1% isoamyl alcohol would provide $55.1 \text{ L}\cdot\text{day}^{-1}$ of isoamyl alcohol, which could subsequently yield approximately 75.3 L or $65.9 \text{ kg}\cdot\text{day}^{-1}$ of isoamyl acetate through esterification. The fractional distillation system, therefore, provides not only the desired purity but also a production rate that fulfills and exceeds the intended process design requirements.

To validate product quality, a sample of the purified isoamyl alcohol was submitted to Intertek, an internationally accredited organization for analytical testing and certification. The analysis confirmed several physicochemical properties: a refractive index of 1.4065, the absence of turbidity, and a measured acidity equivalent to $28 \text{ mg}\cdot\text{L}^{-1}$ of acetic acid. The specific gravity was found to be 0.8083. Heavy metal content, including Pb, As, Cd, and Hg, was below $1 \text{ mg}\cdot\text{kg}^{-1}$, indicating a high level of product safety. Most notably, gas chromatography with flame ionization detection (GC–FID) confirmed that the isoamyl alcohol possessed a purity of 99.61%, demonstrating that the product can be directly used for esterification with acetic acid to synthesize isoamyl acetate without requiring any further purification.

Overall, the pilot-scale fractional distillation system demonstrated excellent separation capability, stability, and high product recovery efficiency. The high purity of the isoamyl alcohol obtained, combined with its favorable physicochemical properties, confirms the suitability of the system for supporting downstream isoamyl acetate production using reactive distillation.

4.2 Laboratory-Scale Study of the Esterification Reaction

4.2.1 Selection of an Appropriate Heterogeneous Catalyst for Isoamyl

Acetate Synthesis

To design an efficient esterification system suitable for the objectives of this research project, the first step involved the selection and evaluation of appropriate heterogeneous catalysts. The esterification reaction between acetic acid and high-purity isoamyl alcohol obtained from the fractional distillation process described in (Section 4.1) was conducted to screen the catalytic performance of four commercially available solid acid catalysts.

The catalysts selected for comparison in this study were AMBERLYST™ 15 E (Rohm & Haas, USA), Tulsion® T-66 MP (Thermax, India), Tulsion® T-63 MP (Thermax, India), and Indion 190 (Ion-Exchange India Ltd., Mumbai). These catalysts were chosen due to their strong Brønsted acidic sulfonic functional groups ($-\text{SO}_3\text{H}$), widespread industrial applications in esterification processes, and their potential suitability for later use in reactive distillation systems. The screening experiments were designed to evaluate not only catalytic activity but also catalyst stability, durability, and the possibility of regeneration after use. Particular emphasis was placed on AMBERLYST™ 15 E due to its established performance in esterification and reactive distillation processes in previous studies. All catalysts were tested under identical reaction conditions to ensure fair comparison. The results from this catalyst screening provided essential information for identifying the most suitable catalyst for subsequent kinetic studies, parameter sensitivity analysis, and pilot-scale reactive distillation experiments. Figure 12. illustrates the catalytic performance of the selected heterogeneous catalysts under identical esterification conditions. All experiments were conducted using 15 wt% catalyst loading, agitation at 200 rpm, and a reaction temperature of 70 °C. The molar ratio of isoamyl alcohol to acetic acid was fixed at 1:3, with isoamyl alcohol designated as the limiting substrate and acetic acid as the excess substrate. For example, in a typical 1-kg reaction mixture, the feed consisted of 312.29 g isoamyl alcohol, 637.52 g acetic acid, and 50.00 g catalyst.

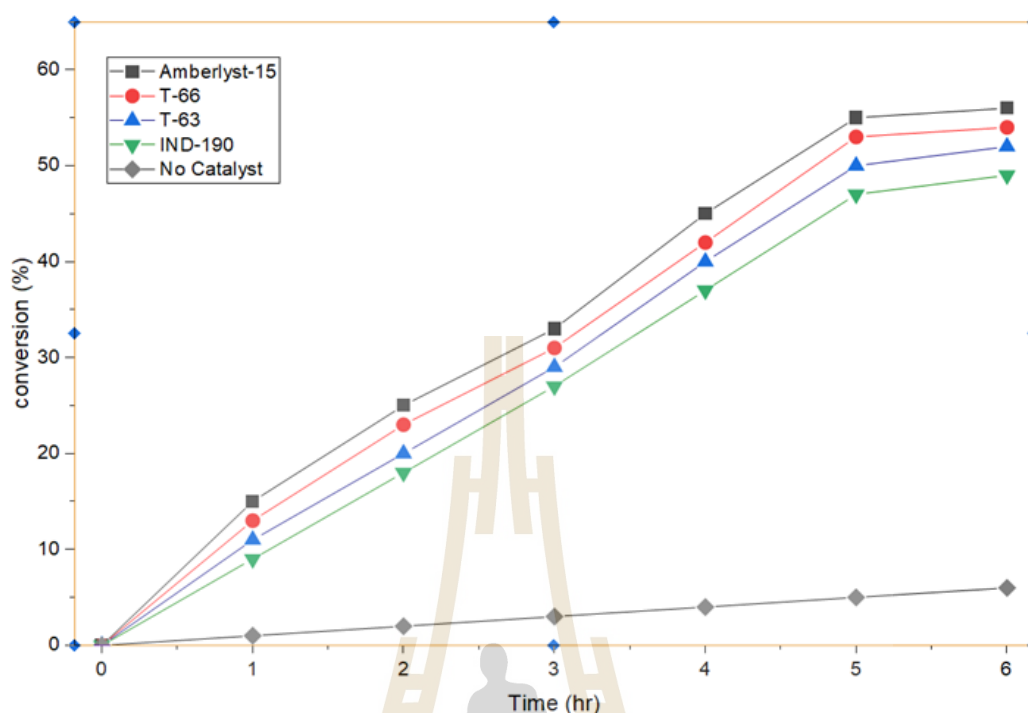


Figure 12. Comparison of catalyst performance.

Samples were withdrawn every hour over a 6-hour reaction period and analyzed for isoamyl acetate formation. The results are reported as conversion (%), defined as the percentage of isoamyl acetate produced relative to the theoretical maximum assuming complete conversion of isoamyl alcohol. The experimental results indicate that all four heterogeneous catalysts were capable of promoting the forward esterification reaction to yield isoamyl acetate. The reaction rate was highest during the first three hours, after which the rate decreased noticeably beyond the fourth hour. The system approached equilibrium after approximately five hours, and no further increase in product yield was observed in the sixth hour. The maximum conversions achieved by each catalyst were as follows: AMBERLYST™ 15E (60%), Tulsion® T-66MP (55%), Tulsion® T-63MP (50%), and Indion 190 (48%). The plateau in conversion is attributed to the accumulation of water, a by-product of esterification, which promotes the reverse hydrolysis reaction and thus limits the forward reaction at equilibrium.

Among all catalysts tested, AMBERLYST™ 15E demonstrated the highest catalytic activity, the fastest reaction rate, and the greatest equilibrium conversion. Moreover, AMBERLYST™ 15E is well-documented in literature for its excellent performance in esterification and related acid-catalyzed reactions, further supporting its selection. Consequently, AMBERLYST™ 15E was chosen as the primary catalyst for subsequent kinetic studies and reactive distillation experiments in this research.

In contrast, the control experiment conducted without a catalyst resulted in only ~5% conversion after six hours, confirming that the reaction proceeds very slowly in the absence of an acid catalyst and highlighting the essential role of solid acid catalysis in isoamyl acetate production.

4.2.2 Effect of Reaction Temperature on Isoamyl Acetate Synthesis

The influence of reaction temperature on the esterification of isoamyl alcohol with acetic acid was investigated using an ion-exchange resin catalyst. Temperature is one of the most critical parameters governing esterification kinetics, as it directly affects molecular mobility, collision frequency, and the equilibrium position of the reaction. Experiments were conducted at temperatures ranging from 60 to 100 °C to identify conditions that provide high conversion while maintaining product quality. Figure 15. shows that increasing temperature significantly enhanced the reaction rate, particularly within the first three hours, during which the steepest rise in conversion was observed. After the fourth hour, the rate gradually declined, and the system approached equilibrium after approximately five hours. The maximum conversions obtained at 60, 70, 80, 90, and 100 °C were 50%, 55%, 60%, 70%, and 75%, respectively, demonstrating that higher temperatures consistently favored ester formation. However operating at excessively high temperatures induced undesirable side reactions. At 100 °C. the reaction mixture developed a noticeable yellow coloration **Figure 13.**likely due to thermal degradation or oxidative by-products, which is undesirable for applications requiring high-purity isoamyl acetate. Moreover, ion-exchange resins possess an upper thermal stability limit of approximately 120 °C, beyond which structural degradation may occur.

Considering both conversion efficiency and product integrity, a moderate temperature is preferred. Therefore, 70 °C was selected as the optimal reaction temperature for subsequent kinetic studies and process development, as it provided satisfactory conversion while preventing discoloration and minimizing thermal stress on the catalyst.

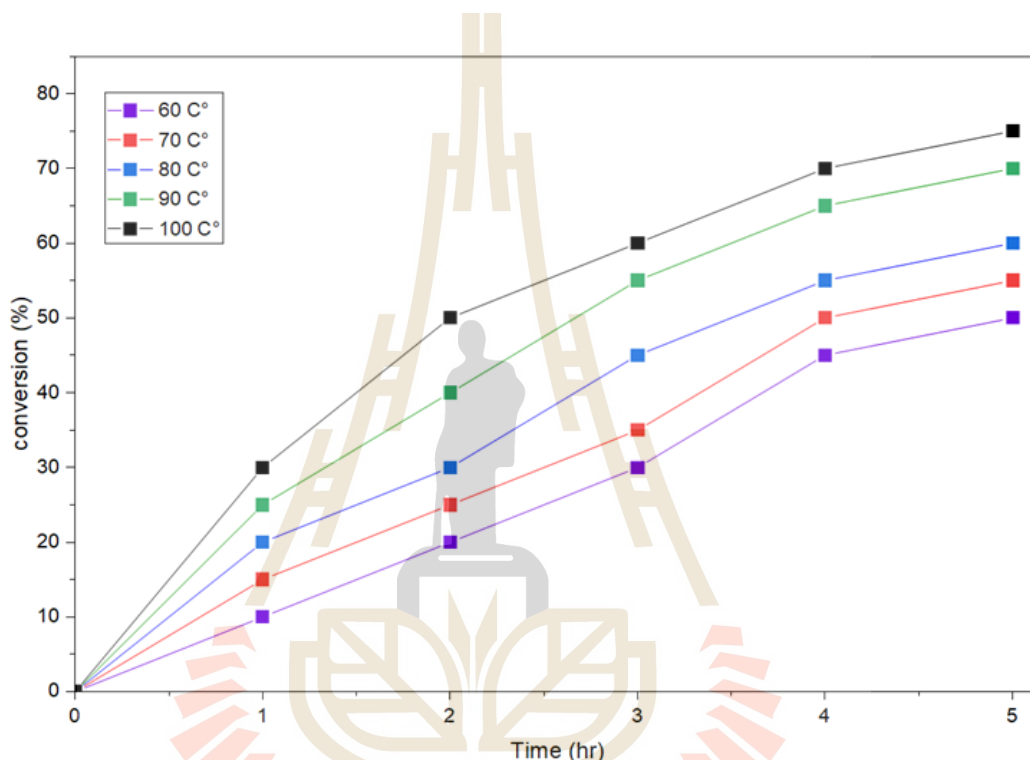


Figure 13. Effect of temperature on the esterification reaction.

4.2.3 Effect of Catalyst Mass on Esterification Performance

Catalyst loading plays a critical role in determining the rate and extent of esterification reactions. An increase in catalyst mass typically enhances the availability of active sites, thereby accelerating the reaction and increasing the overall conversion. As shown in Figure 16, higher catalyst loadings (5%, 10%, and 15% w/w) consistently resulted in higher conversions over time, with all reactions progressing steadily until reaching equilibrium at approximately five hours. At a catalyst loading of 15%, the reaction exhibited the highest productivity, with a maximum rate of approximately 25%

conversion per hour during the early reaction period. In contrast, the 5% loading yielded a lower productivity of around 15% conversion per hour.

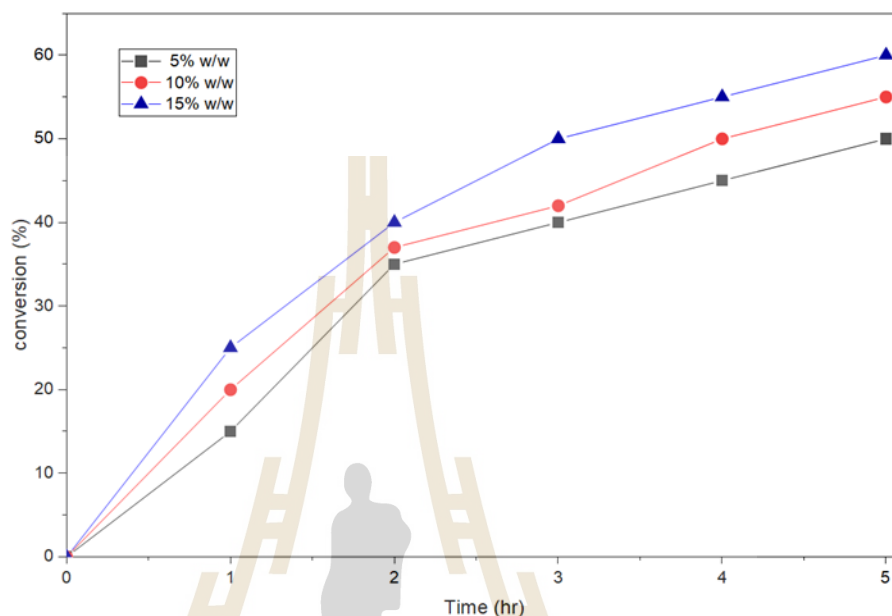


Figure 14. Influence of catalyst loading at different concentrations.

At a catalyst loading of 15%, the reaction exhibited the highest productivity, with a maximum rate of approximately 25% conversion per hour during the early reaction period. In contrast, the 5% loading yielded a lower productivity of around 15% conversion per hour. Although larger quantities of catalyst significantly enhance the reaction rate, the improvement in final conversion was relatively modest. After five hours, conversions were approximately 50% for the 5% loading and 60% for the 15% loading—only a 10% difference despite a threefold increase in catalyst mass.

Given that catalyst consumption directly influences capital expenditures (CAPEX) and long-term operating costs, optimizing catalyst use is essential for economic feasibility. Excessive catalyst loading may offer diminishing returns in conversion improvement while significantly increasing investment and replacement costs.

Considering both reaction performance and cost efficiency, a 5% catalyst loading was selected as the optimal condition for subsequent experiments. This

loading was sufficient to achieve 50% conversion within five hours near the equilibrium limit while minimizing catalyst usage. Overall, the results indicate that increasing catalyst mass enhances reaction kinetics by providing more active sites for substrate interaction; however, the equilibrium conversion remains similar across catalyst loadings, and economic factors justify the use of lower catalyst quantities.

4.2.4 Effect of the Initial Molar Ratio on Esterification Performance

The initial molar ratio of reactants is a key parameter influencing the conversion in esterification reactions. In this study, isoamyl alcohol was designated as the limiting reactant, while acetic acid was supplied in excess to drive the reaction toward isoamyl acetate formation. Under stoichiometric conditions, the reaction proceeds at a 1:1 molar ratio (with molecular weights of 88 g/mol for isoamyl alcohol and 60 g/mol for acetic acid).

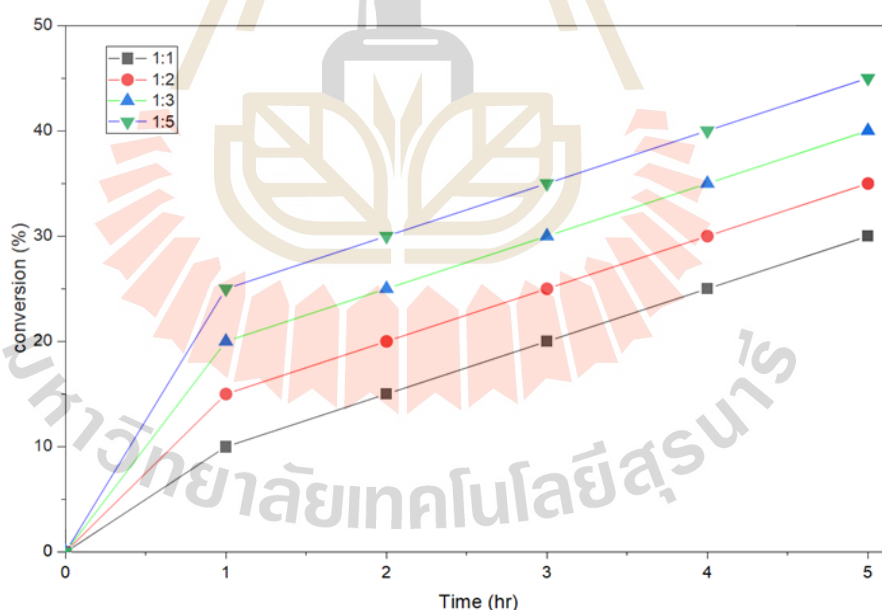


Figure 15. Effect of the initial molar ratio of reactants on the esterification reaction.

However, increasing the molar ratio of acetic acid generally enhances conversion by shifting the reaction equilibrium forward. To investigate this effect, the molar ratio of isoamyl alcohol to acetic acid was varied from 1:1 to 1:5. As shown in

Figure 17. increasing the acetic acid ratio resulted in higher conversions, particularly between molar ratios of 1:1 and 1:3. Beyond a ratio of 1:3, however, the enhancement in conversion became less significant.

This diminishing effect can be attributed to over-dilution, where excessively high acetic acid concentrations (e.g., at 1:5) reduce the effective concentration of the limiting reactant, thereby slowing reaction kinetics. Because the reaction rate depends strongly on substrate concentrations, dilution effects counteract the benefit of increased acetic acid. Moreover, as an equilibrium-limited reaction, esterification generates water as a by-product. Increasing the initial molar ratio also increases the amount of water formed, which in turn promotes the reverse hydrolysis reaction, keeping conversions below 50% across all experiments. In addition, a higher excess of unreacted acetic acid imposes unnecessary load on downstream separation, particularly in the distillation steps, thereby increasing energy demand and operational cost.

Considering both reaction performance and downstream process efficiency, a molar ratio not exceeding 1:2 was selected for subsequent experiments as the optimal balance between conversion enhancement, reaction kinetics, and process economics.

4.3 Aspen Plus Simulation

Aspen Plus V14 was employed to simulate the reactive distillation (RD) process with the objective of identifying optimal operating conditions for maximizing isoamyl acetate (IAAc) production.

The simulation model incorporated the actual pilot-scale column specifications, consisting of 30 theoretical stages with a catalytic reaction zone located between Stages 10 and 20. Feed introduction was assigned according to component volatility: acetic acid (AA) at Stage 10 and isoamyl alcohol (IAA) at Stage 15. The NRTL thermodynamic model was selected due to its strong reliability in representing highly non-ideal, partially miscible systems such as alcohol–acid–ester mixtures. UNIQUAC

was used as a cross-validation method. Table 7. summarizes the key column specifications and input parameters used in the simulation, including feed flow rates (IAA: 0.2366 kmol·h⁻¹; AA: 0.1922 kmol·h⁻¹), reflux ratio (2.1), and temperature of feed streams (100 °C).

Table 7. Column specifications and other parameters used for simulations.

component	parameter
Feed Temperature	100 C
Pressure	1 atm
Total Stages	30
Reactive zone	10-20
Feed Stage	
acetic acid	Above 10
isoamyl alcohol	Above 20
Mass flow (kmol/h)	
acetic acid	0.1922
isoamyl alcohol	0.2366
Reflux Ratio	2.1
Property method	NTRL

Reaction kinetics were integrated based on laboratory-derived rate constants, allowing the model to accurately capture the coupling between mass transfer and chemical reaction.

4.4 Enhancement of Esterification Performance Using Reactive

Distillation

Figure 16. illustrates the structured packing configuration used in the reactive distillation column. The use of structured packing in a catalytic distillation reactor improves both reaction performance and mass transfer efficiency due to its ordered internal geometry, which promotes uniform liquid distribution and efficient heat

transfer. Compared with random packing, structured packing provides significantly lower pressure drop and more controlled temperature gradients, resulting in enhanced catalyst effectiveness and higher product yield. The pilot-scale reactive distillation column employed in this study has a total height of 5.0 meters and operates in continuous mode. Acetic acid (from the acid feed tank) and isoamyl alcohol (from the alcohol feed tank) are introduced at different locations within the reaction zone based on their boiling points. Acetic acid, having a lower boiling point, is fed into the lower section of the reaction zone, while isoamyl alcohol—characterized by a higher boiling points introduced into the upper section.

The reaction zone consists of a stainless-steel column with a diameter of 3 inches and a height of 1 meter. This zone is packed with ten units of Katapak-SP (Sulzer Chemtech, Switzerland), each containing 100 g of AMBERLYST™ 15E, resulting in a total catalyst loading of 1 kg. The packing elements are designed with multi-layer stainless-steel mesh folded into structured channels that create void spaces for catalyst placement. The geometric arrangement prevents excessive tightness between layers, ensuring uniform gas–liquid distribution and minimizing pressure drop across the bed.

During operation, the reactor receives liquid feed while hot vapor rises from the reboiler at the bottom, establishing a counter-current flow regime. Vapor flowing upward contacts the descending liquid across the structured packing, allowing simultaneous reaction and separation. The upper (rectifying) and lower (stripping) sections of the column consist of transparent glass cylinders with a diameter of 3 inches. Each section contains perforated trays equipped with 10-mm downcomer pipes and 1-cm weirs to control liquid flow and maintain stable hydrodynamics within the distillation column. the batch esterification performance between isoamyl alcohol and acetic acid, which proceeds via a second-order reversible reaction, producing isoamyl acetate as the primary product and water as a by-product. At the beginning of the experiment, the reactants—acetic acid (50 mol) and isoamyl alcohol (35 mol)—were charged into the reactor. The reaction mixture was continuously circulated from the bottom of the reactor to the top of the packed column to ensure effective contact with the catalyst. Positioning the solid catalyst within the center of the column

provides several advantages: the resin beads remain stationary, minimizing mechanical attrition and fragmentation, and both reactants had already been purified in earlier steps. Additionally, conducting the reaction at 70 °C, well below the thermal degradation limit of ion-exchange resins, is expected to prolong catalyst lifetime.

4.4.1 Batch Esterification



Figure 16. Katapak-SP structured packing used for loading AMBERLYST™ 15E catalyst.

At the initial stage of the reaction, the concentrations of both reactants were high, while isoamyl acetate and water were absent. Immediately after the reaction commenced, the concentrations of both products increased. Between 2 and 6 hours, the concentrations of the reactants decreased rapidly, indicating fast forward reaction activity, while isoamyl acetate and water increased accordingly.

After approximately 6 hours, the system approached chemical equilibrium, with acetic acid and isoamyl alcohol decreasing to approximately 30 and 10 mol, respectively, while isoamyl acetate and water stabilized at around 20 mol. This plateau behavior signifies that the forward and reverse reaction rates had become equal. The

concentration profiles observed are characteristic of reversible esterification reactions. To further enhance conversion beyond this equilibrium limit, process intensification strategies such as in-situ water removal through reactive distillation are required. This is expected to significantly increase isoamyl acetate yield in the integrated reactive distillation system evaluated in this study.

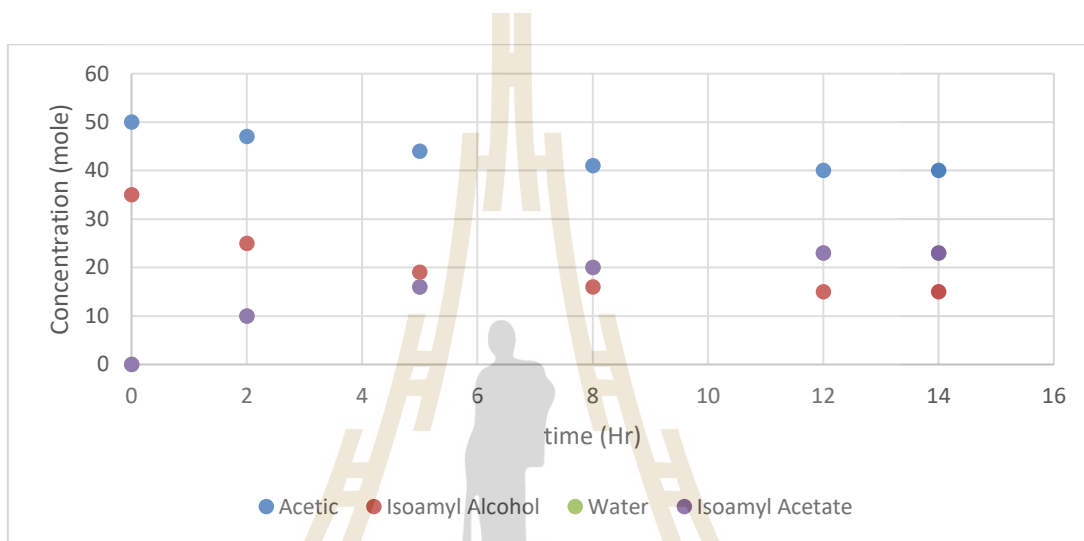


Figure 17. the batch esterification performance.

4.4.2 Enhancement of Esterification Yield Using Semi-Batch Reactive Distillation

the experimental results of the semi-batch reactive distillation process for the esterification of isoamyl alcohol (IAA) and acetic acid (AA), producing isoamyl acetate (IAAc) as the main product and water as the by-product. During the initial stage (0–6 h), the system was operated without water removal. Throughout this period, the concentrations of acetic acid (initially 50 mol) and isoamyl alcohol (35 mol) gradually decreased, while the concentrations of isoamyl acetate and water steadily increased, reflecting normal forward esterification behavior. However, as the reaction proceeded, the accumulation of water became pronounced. The increased water content enhanced the reverse hydrolysis reaction, thereby limiting the overall conversion due to the reversible nature of the esterification equilibrium. To overcome this limitation, water removal was initiated after the 6th hour using vacuum distillation at 200 mBar.

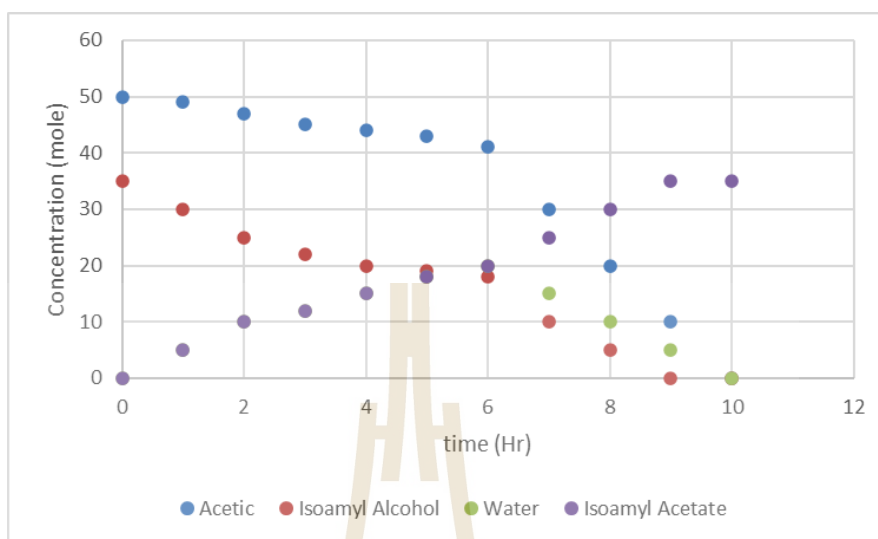


Figure 18. the experimental results of the semi-batch reactive distillation process.

This operation resulted in a marked decrease in water concentration, as clearly illustrated in the graph. The removal of water significantly suppressed the reverse reaction and shifted the equilibrium toward product formation. Consequently, the concentration of isoamyl acetate increased rapidly, while the concentrations of acetic acid and isoamyl alcohol continued to decline. In the period between 8–10 hours, the concentrations of both reactants approached near-zero levels, indicating almost complete consumption and demonstrating highly efficient conversion under reactive distillation with water removal.

The substantial increase in isoamyl acetate concentration confirms the effectiveness of equilibrium shifting via in-situ water removal—one of the primary advantages of reactive distillation. By eliminating the equilibrium constraint, the forward reaction is greatly enhanced, enabling high yield production. After complete water removal, the remaining step involved fractional distillation to separate the residual acetic acid from the product stream. The purified isoamyl acetate obtained exhibited a high purity of 99.99%, with a total volume of approximately 75 L, meeting the specifications outlined in Objective 3 of the project. Potential side reactions, including dehydration and etherification, were also considered. These reactions typically require severe operation conditions (e.g., 150 °C and 40 bar for dehydration,

and 115 °C for etherification over 24 h), as reported in previous studies. To avoid such undesired pathways, the present work operated under mild conditions—specifically temperatures not exceeding 70 °C and total reaction time below 8 hours. As a result, no discoloration or degradation of the product was observed.

Furthermore, catalyst reusability tests demonstrated consistent performance of AMBERLYST™ 15E over at least five consecutive cycles, indicating good stability and suitability for long-term operation in reactive distillation systems.

4.5 Mathematical Modeling and Simulation: Mass and Energy Balance

Analysis

From Figure 21. illustrates the temperature distribution along the reactive distillation (RD) column during the esterification of isoamyl alcohol with acetic acid to produce isoamyl acetate. Both experimental data and simulation results derived from Aspen Plus are presented for comparison. The temperature profile provides critical insight into reaction separation coupling, catalyst zone performance, and vapor–liquid equilibrium (VLE) behavior inside the RD system. In the reaction zone (Stages 10–20), the experimental temperature ranges from approximately 114 to 120 °C, which closely matches the simulation predictions. This temperature window corresponds to the operational range in which the esterification reaction proceeds effectively in the presence of the solid acid catalyst (AMBERLYST™ 15E). The slight increase and subsequent stabilization of temperature in this zone reflect the balance between heat generated by the exothermic esterification reaction and heat absorbed during vaporization. The simulation accurately captures this behavior, indicating that the kinetic and thermodynamic models used primarily NRTL for VLE and a reversible second-order rate expression are appropriate for describing the system.

The relatively flat temperature plateau observed in the middle stages corresponds to the catalyst-packed section (Katapak-SP). In this region, both reaction and mass-transfer processes occur simultaneously. The minimized deviation between

experimental and predicted temperatures (typically $<3\text{ }^{\circ}\text{C}$) suggests that the liquid holdup, effective interfacial area, and catalyst activity were well represented in the model. This reinforces the suitability of the structured packing design, which enhances vapor–liquid contact and drives both the reaction forward and separation efficiency upward. At the upper stages of the column (rectifying section), temperatures are lower due to the presence of lighter components such as isoamyl alcohol, acetic acid, and trace water. Experimental temperatures are slightly higher than simulation predictions, likely due to heat losses not accounted for in the model and minor fluctuations in reflux ratio in real operation.

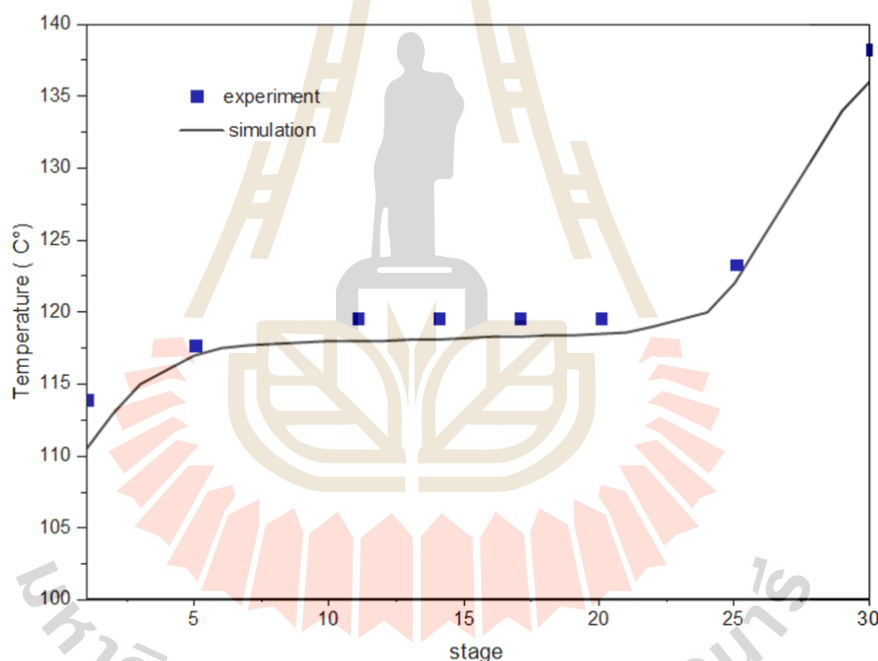


Figure 9. Temperature profile in the reactive distillation column.

Toward the bottom stages (stripping section), temperatures rise sharply to approximately $135\text{--}138\text{ }^{\circ}\text{C}$ in the experimental data, approaching the boiling point of isoamyl acetate and the heavier residual components. The simulation follows a similar trend but predicts a somewhat smoother temperature increase. This discrepancy may stem from imperfect insulation of the reboiler or the presence of trace heavier by-products in the experimental system. However, the general trend

remains consistent, confirming that the RD system effectively separates isoamyl acetate from unreacted alcohol. Overall, the strong alignment between simulation and experiment validates the accuracy of the RD model for predicting temperature behavior in the isoamyl acetate system. The model can reliably be used for further optimization, including energy minimization, evaluation of reflux ratio, and determination of optimal feed-stage placement. The temperature profile also confirms the successful integration of reaction and separation, which is essential for achieving high conversion and product purity in reactive distillation systems.

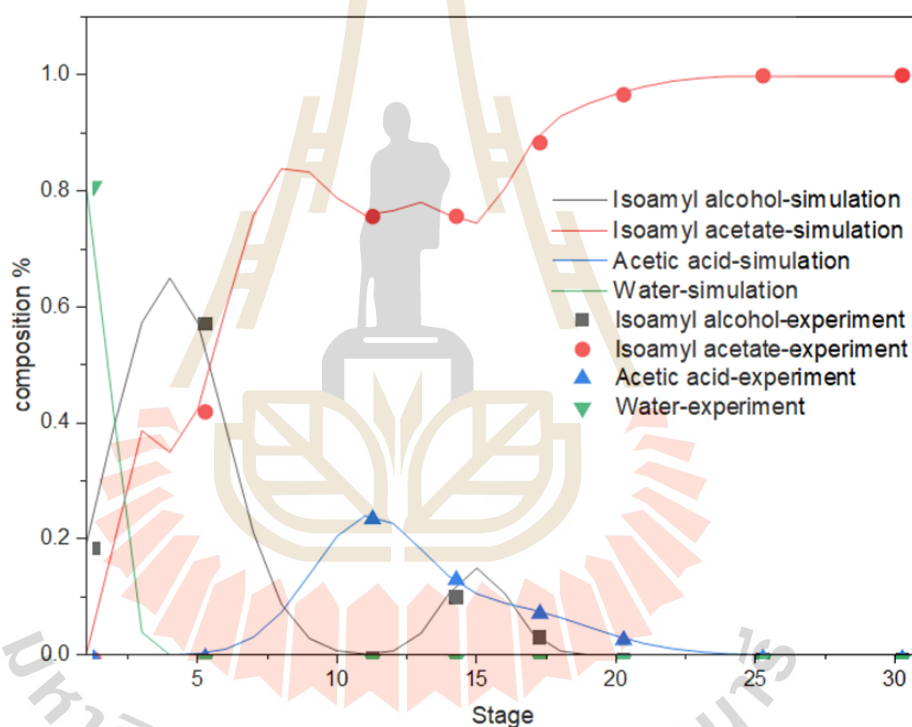


Figure 10. Stage-wise variation of compositions for reactive distillation.

Figure 22. presents the stage-wise composition profiles of isoamyl alcohol, acetic acid, isoamyl acetate, and water obtained from both experimental measurements and steady-state simulation using Aspen Plus. These profiles provide critical insight into the coupling between chemical reaction and mass transfer within the reactive distillation (RD) system, as well as the efficiency of the structured packing (Katapak-SP) in promoting simultaneous reaction and separation.

The simulation results demonstrate that isoamyl alcohol concentration is highest in the upper stages of the column, reflecting its higher boiling point and the introduction of the alcohol feed above the reaction zone. Experimentally, isoamyl alcohol displays a similar decreasing trend along the column, with the highest concentration detected at the feed region and diminishing sharply toward the lower stages. This behavior is consistent with its consumption in the catalytic esterification reaction and its downward transport by liquid flow. The strong agreement between simulation and experiment indicates appropriate representation of vapor–liquid equilibrium (VLE) and reaction kinetics in the model.

Isoamyl acetate the desired ester product exhibits an increasing concentration profile from the lower to the upper stages. The simulation predicts a smooth rise in product concentration, reaching its maximum near the top of the reaction zone and rectifying section. Experimental data confirm this trend, showing high product composition from Stage 10 onward and approaching nearly pure isoamyl acetate in the uppermost stages. This reflects the efficient removal of the product through vapor up flow and its stability under the reaction conditions. The close matching between the datasets validates the effectiveness of the catalyst distribution and the overall RD configuration. Acetic acid shows the opposite behavior: its concentration is highest in the lower stages—where the acid feed enters—and gradually decreases as it is consumed through reaction and as lighter components vaporize. Both simulation and experimental profiles confirm that the acid is mostly depleted within the catalyst-packed stages, demonstrating that the reaction zone is properly sized and that mass transfer between phases is sufficient to sustain the forward esterification reaction.

Water, generated as a by-product, shows a sharp concentration peak in the lowest stages. In the simulation, water forms predominantly near the bottom of the reaction zone due to its low volatility and is subsequently removed through the reboiler. Experimental results show a similar pattern, with water concentration rapidly declining beyond the first few stages. The small deviations between the two datasets likely arise from transient water accumulation during the early operation of the vacuum-assisted system, which is not fully captured in the steady-state model.

Overall, the stage-wise composition profiles confirm that the reactive distillation system performs as intended: reactants are brought into close contact in the catalyst-packed zone, products are effectively removed to shift the equilibrium forward, and the by-product water is expelled at the column bottom. The strong agreement between experimental and simulation data validates the accuracy of the kinetic and thermodynamic models used, confirming their suitability for further optimization of column operating conditions, energy consumption, and design scale-up.

4.6 Isoamyl Acetate Production Process in Pilot Scale

Fusel oil, a dark-brown by-product generated from ethanol fermentation, was valorized as the feedstock for isoamyl acetate production in a pilot-scale process. The process design comprised sequential separation and reactive distillation units to recover, purify, and convert isoamyl alcohol into a high-value ester. The raw fusel oil was first introduced into column D-101, where fractional distillation was employed to separate isoamyl alcohol from other components such as water, ethanol, propanol, and iso-butanol. This step is critical because it transforms a heterogeneous waste stream into a concentrated feed of isoamyl alcohol (>95% purity). The mass and energy balance confirmed that isoamyl alcohol was recovered at ~33.5 kg/h with high purity, while light components and water were removed in overhead streams. The isoamyl alcohol obtained from D-101 was further purified in column D-102 to remove color bodies, aldehydes, and oxygenated impurities that contribute to the brown appearance and instability of the fusel oil fraction. This polishing step produced a clear, colorless isoamyl alcohol stream, which is essential for downstream esterification. The clarity of the feedstock not only ensures a product that meets commercial

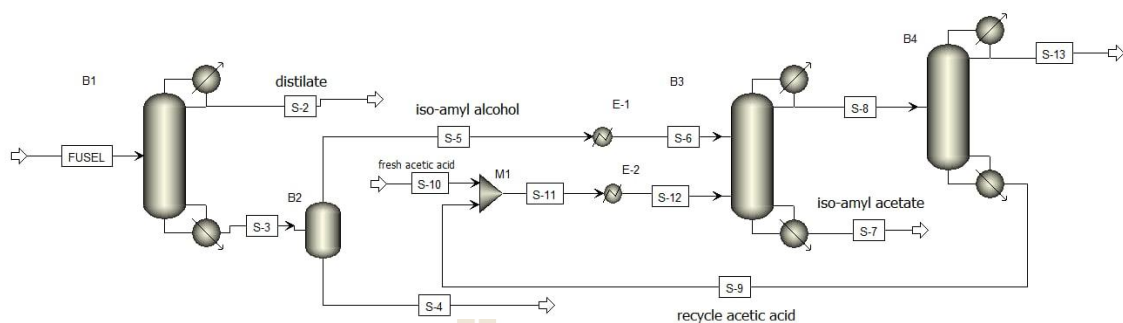


Figure 23. Process flowsheet of the isoamyl acetate production process in pilot scale.

Table 8. Mass balance of the isoamyl acetate (Fuseloil-S6)

COMPONENT	fusel oil	S2	S3	S4	S5	S6
Water	10.20	10.20	0.00	0.00	0.00	0.00
Propanol	6.00	5.94	0.06	0.06	0.00	0.00
1-Butanol	0.36	0.36	0.00	0.00	0.00	0.00
Iso-Butanol	6.00	6.00	0.00	0.00	0.00	0.00
Iso-Amyl Alcohol	33.84	0.34	33.50	0.03	33.47	33.47
Ethanol	3.60	3.60	0.00	0.00	0.00	0.00
Acetic Acid	0.00	0.00	0.00	0.00	0.00	0.00
Iso-Amyl Acetate	0.00	0.00	0.00	0.00	0.00	0.00
total mass flow Kg/hr	60.00	26.44	33.56	0.09	33.47	33.47
Temperature/ C	100.00	85.66	129.27	107.58	130.67	100.00
Pressure atm	1	1	1	1	1	1
Mass Enthalpy KJ/KG	-4.50E+03	-7.42E+03	-3.78E+03	-4.25E+03	-3.76E+03	-3.86E+03
Enthalpy Flow KJ/hr	-1.90E+07	-5.70E+06	-1.30E+07	-3.45E+05	-1.30E+07	-1.30E+07

Quality specifications but also prevents side reactions and catalyst deactivation during esterification. the purified isoamyl alcohol was then introduced into the reactive distillation column together with acetic acid. Under optimized conditions (70–80 °C, 10 wt% Amberlyst-15E, 1:2 molar ratio), isoamyl acetate was formed while water was continuously removed in the distillate. This integration of reaction and separation shifted the equilibrium toward ester formation, yielding ~44.3 kg/h of isoamyl acetate (Stream S7) at high purity (~95%).

Excess acetic acid appearing in recycle streams (S8–S12) can be recovered and reused, further improving resource efficiency.

This process demonstrates the transformation of fusel oil—a low-value, colored by-product into isoamyl acetate, a high-value ester widely used in food flavoring, fragrance, and solvents. The use of reactive distillation reduces energy consumption by approximately 30% compared with a conventional batch + separation sequence. At the same time, the process minimizes wastewater generation (only ~6.1 kg/h in S13) and enables acid recycling, thereby lowering environmental burden. Thus, the pilot-scale operation validates both the economic viability and environmental advantages of fusel-oil valorization through process intensification.

Table 9. Mass balance of the isoamyl acetate (S7–S6)

COMPONENT	S7	S8	S9	S10	S11	S12	S13
Water	0.00	6.14	0.00	0.00	0.00	0.00	6.14
Propanol	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-Butanol	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Iso-Butanol	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Iso-Amyl Alcohol	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ethanol	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Acetic Acid	0.54	69.00	69.00	21.00	90.00	90.00	0.00
Iso-Amyl Acetate	44.33	0.00	0.00	0.00	0.00	0.00	0.00
total Kg/hr	44.87	75.14	69.00	21.00	90.00	90.00	6.14
Temperature/ °C	96.25	86.27	118.12	100.00	100.00	100.00	87.83
Pressure atm	1	1	1	1	1	1	1
Mass Enthalpy KJ/KG	-6.0E+03	-8.06E+03	-7.40E+03	-7.51E+03	-7.51E+03	-7.51E+03	-8.27E+03
Enthalpy Flow KJ/hr	-5.5E+07	-3.15E+02	-8.01E+01	-4.10E+07	-4.10E+07	-4.10E+07	-2.34E+02

CHAPTER V

CONCLUSION

This study demonstrates a comprehensive and scalable approach for upgrading fusel oil, an ethanol-fermentation byproduct, into high-value isoamyl acetate through an integrated process combining fractional distillation, heterogeneous catalysis, and reactive distillation. Pilot-scale fractional distillation effectively produced high-purity isoamyl alcohol (>99%) with a recovery exceeding 95%, establishing its suitability as a feedstock for esterification. Catalyst screening identified Amberlyst™ 15E as the most efficient and robust solid acid catalyst, providing superior conversion and stability under the tested conditions.

Reactive distillation significantly intensified the esterification process by simultaneously removing the byproduct water and driving the reaction toward completion. Using structured packing (Katapak-SP) filled with Amberlyst™ 15E, the system achieved >96.9% purity and >95% yield of isoamyl acetate within 8 hours, demonstrating excellent process performance. Thermodynamic modeling using NRTL and UNIFAC further validated the mass and energy balances and supported accurate prediction of phase behavior for process optimization.

Overall, the integrated process enabled the production of approximately 60 kg day⁻¹ ($\approx 68 \text{ L day}^{-1}$) of high-purity isoamyl acetate, surpassing the initial design target and confirming the technical and economic viability of the approach. These results highlight the potential for transforming low-value fusel oil into a commercially valuable ester through a sustainable, intensified, and industry-relevant process. The findings provide a strong foundation for future industrial scale-up and contribute meaningfully to circular bioeconomy strategies aimed at valorizing fermentation side-streams.

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APPENDIX

The rate constant is determined using the Arrhenius equation:

$$k = k_0 \cdot \exp(-E_a / (R \cdot T))$$

Given:

$$- k_0 = 2.1 \times 10^3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$$

$$- E_a = 45,000 \text{ J/mol}$$

$$- T = 353 \text{ K}$$

$$- R = 8.314 \text{ J/mol} \cdot \text{K}$$

$$k = 4.68 \times 10^{-4} \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$$

Equilibrium Constant

$$K_{eq} = \exp(-\Delta G^\circ / (R \cdot T))$$

$$\text{Given: } - \Delta G^\circ = -28,500 \text{ J/mol}$$

$$- T = 353 \text{ K}$$

$$- K_{eq} = 1.63 \times 10^4$$

Vapor-Liquid Equilibrium Calculation

Raoult's Law:

$$y_i \cdot P = x_i \cdot \gamma_i \cdot P_i^*$$

Given for isoamyl alcohol:

$$- \gamma = 2.10$$

$$- P_i^* = 55.2 \text{ kPa}$$

$$- P = 101.3 \text{ kPa}$$

$$y_i = 0.458$$

Minimum Theoretical Stages (Fenske Equation)

$$N_{\min} = \ln[(x_D/(1-x_D)) / (x_B/(1-x_B))] / \ln(\alpha)$$

Given:

$$- x_D = 0.96$$

$$- x_B = 0.02$$

$$- \alpha = 2.8$$

$$N_{\min} = 6.86 \text{ stages}$$

Reboiler Duty

$$Q_R = m \cdot H_v$$

Given:

$$- m = 0.017 \text{ kg/s}$$

$$- H_v = 410 \text{ kJ/kg}$$

$$Q_R = 6.97 \text{ kW}$$

Condenser Duty

$$Q_C = m \cdot H_v$$

Given:

- $m_{\text{v}} = 0.009 \text{ kg/s}$

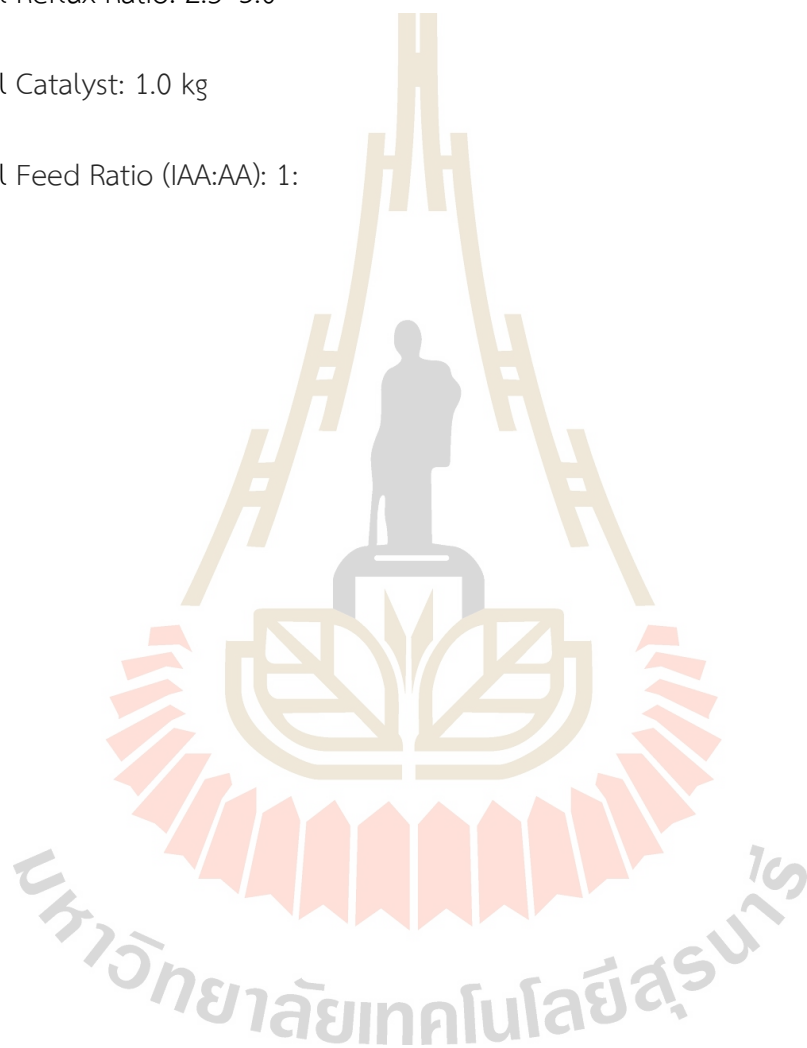
- $H_{\text{v}} = 2257 \text{ kJ/kg}$

$Q_{\text{C}} = 20.3 \text{ kW}$

Optimal Reflux Ratio: 2.5–3.0

Optimal Catalyst: 1.0 kg

Optimal Feed Ratio (IAA:AA): 1:



BIOGRAPHY

Mr. Chanathip Somsrang was born on 2 March 2000 in Kaeng Sanam Nang District, Nakhon Ratchasima Province, Thailand. He completed his Bachelor of Engineering (Chemical Engineering) from Suranaree University of Technology, Nakhon Ratchasima, in 2024. He is currently pursuing a Master's degree in Biotechnology at Suranaree University of Technology.

