

Effect of Different Alcohol Chain Lengths, Degree, Branching and Type of Solvent used on the Yield of Esters using Esterfication

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Abstract

Esterfication involves the chemical reaction between a carboxylic acid and an alcohol to produce water and an ester. This study specifically examined how the structure of the alcohol—including its chain length and degree of branching—alongside the choice of catalyst and solvent, dictates the final ester yield. By reviewing the work of Romero et al. on enzymatic production in supercritical carbon dioxide (SC-CO₂) and the research by Sadanandan and Raveendran on SW nanoparticle catalysts, several patterns emerged. Generally, primary alcohols featuring longer, linear chains resulted in superior yields. The choice of solvent also proved critical; while n-hexane outperformed SC-CO₂, cyclohexane, and toluene for shorter or more branched alcohols, SC-CO₂ was equally effective when dealing with longer, straight-chain alcohols. Notably, toluene offered a slight advantage specifically when working with aromatic structures like benzyl alcohol.

Introduction

Esterfication is a fundamental chemical process where a carboxylic acid and an alcohol react—typically aided by a catalyst—to produce esters and water. Because esters are responsible for many of the distinct smells and flavors we encounter, this reaction is a cornerstone of the food, fragrance, and pharmaceutical industries, as well as biofuel production. While traditional strong acids have long been used as catalysts, modern research explores more sustainable options like enzymes or solid acid catalysts, such as tin(IV) tungstate (SW) nanoparticles, which offer better stability and can be reused.

Research Scope and Objectives

The efficiency of these reactions isn't uniform; it fluctuates significantly based on the chemical environment and the structure of the reactants. This research specifically investigates how different variables dictate the final yield:

- **Molecular Structure:** We are comparing how chain length (from short-chain methanol to long-chain octanol) and the degree of the alcohol (primary, secondary, or tertiary) affect the reaction speed and output.
- **Steric Hindrance:** The study examines how branching in iso-alcohols or the presence of bulky aromatic rings in benzyl alcohol can physically "crowd" the reaction site, potentially slowing down the kinetics.
- **Solvent Dynamics:** Different mediums—specifically **n-hexane**, **cyclohexane**, **toluene**, and **supercritical carbon dioxide (SC-CO₂)**—are being analyzed to see how they influence reactant solubility and overall productivity.

Importance-

Refining our understanding of these parameters is about more than just lab curiosity; it's about industrial scaling. By identifying the ideal combination of catalyst and solvent, companies can make ester production more efficient and environmentally friendly. For instance, using SC-CO₂ as a "green" solvent helps eliminate toxic residues, while solid catalysts like **SW nanoparticles** provide a more robust and recyclable alternative to traditional liquid acids.

Methodology

Two distinct experiment approaches were utilised:

- (i) **enzymatic esterification** using Novozyme 435 in supercritical carbon dioxide(SC-CO₂) and n-hexane by paper 1
- (ii) **solid acid-catalysed esterification** using tin(IV) tungstate (SW) nanoparticles in Cyclohexane and Toluene by paper 2

i). Enzymatic esterification:

The researchers used a **50 mL batch reactor** equipped with precise temperature and pressure controls and an agitation speed of **500 rpm**. For the high-pressure runs, a CO₂ feed system maintained the environment at **5 MPa (50 bar)**. To drive the reaction, they used **Novozyme 435**—a reliable immobilized lipase catalyst from *Candida antarctica*.

The process involved:

- **Reactants:** Equimolar concentrations (0.8 M) of acetic anhydride and various alcohols.
- **Catalyst Loading:** 3.3% w/w of the enzyme was added to the mixture.
- **Comparative Baseline:** Identical experiments were mirrored using **n-hexane** at atmospheric

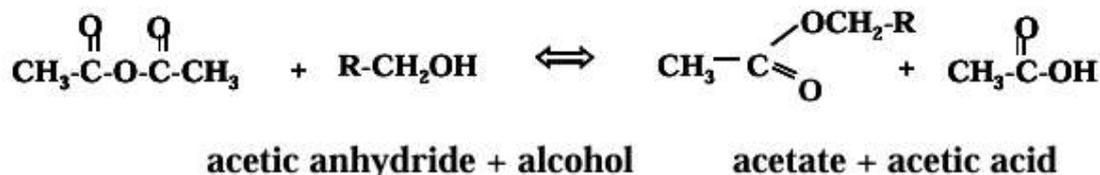
pressure to provide a clear performance benchmark against the SC-CO₂ method.

Analysis and Monitoring

Each reaction was tracked over a **120-minute** window. To determine exactly how much alcohol was converted and to measure the specific production of benzyl acetate, the team utilized two primary analytical techniques:

1. **Gas Chromatography (GC):** Used to monitor general ester conversion. This setup employed helium as a carrier gas (29.5 ml/min) with column temperatures ranging from **75°C to 100°C** depending on the specific compound being analyzed. Both the injector and detector were set to **250°C**.
2. **High-Performance Liquid Chromatography (HPLC):** Specifically used for quantifying benzyl acetate. This involved a **Varian 9050 chromatograph** with a C18 column and a UV detector set to **270 nm**. They used a 50:50 water-to-acetonitrile mobile phase for the gradient elution.

General reaction scheme for the experiment in Paper 1:

**ii). Solid acid-catalysed esterification- Synthesis and Characterization of Tin(IV) Tungstate Nanoparticles-**

The second study centered on the synthesis and characterization of **tin(IV) tungstate (SW) nanoparticles**, which served as a robust solid acid catalyst for the esterification process.

Catalyst Synthesis

To create these nanoparticles, the researchers employed a **chemical co-precipitation method**. The process began with two primary precursors: **tin(IV) chloride (SnCl₄ · 5H₂O)** and **sodium tungstate (Na₂WO₄ · 2H₂O)**. A crucial part of the synthesis was the use of **EDTA (0.02 M)** as a capping agent, which acted as a

chemical "boundary" to control the growth and prevent the particles from becoming too large.

The step-by-step preparation involved:

1. **Mixing:** A 0.2 M solution of tin(IV) chloride was gradually stirred into the aqueous EDTA.
2. **Precipitation:** 0.2 M sodium tungstate was added dropwise while the acidity was tightly controlled, maintaining a **pH of 1–2** using hydrochloric acid (HCl).
3. **Purification:** The resulting gel-like precipitate was filtered and washed thoroughly with distilled water.
4. **Activation:** To ensure the catalyst was in its active hydrogen form, the solid was soaked in 1 M HCl, then dried for final use.

Structural Characterization

Before testing the catalyst in reactions, the team used several advanced analytical tools to "map out" its physical properties:

- **XRD (X-ray Diffraction):** Used to verify the crystalline structure of the particles.
- **Microscopy (SEM & HRTEM):** Scanning Electron Microscopy (SEM) helped observe the surface texture, while High-Resolution Transmission Electron Microscopy (HRTEM) confirmed a very fine particle size of approximately **15–20 nm**.
- **Thermal Analysis (TGA/DTA):** These tests were conducted to ensure the catalyst could withstand the heat of a chemical reactor without breaking down.
- **BET Method:** This analysis measured the surface area, revealing a high specific surface area of **205 to 225 m²/g**. In catalysis, a higher surface area generally translates to more active sites for the reaction to occur.

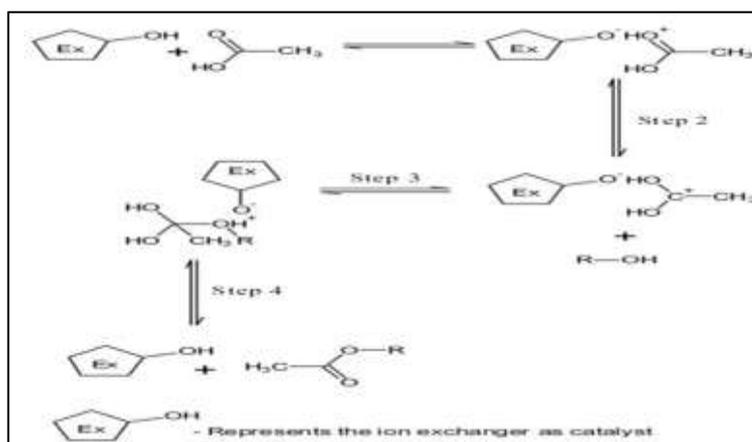
Esterification Utilizing SW Nanoparticles as a Catalyst-

Once the tin(IV) tungstate (SW) nanoparticles were synthesized and characterized, their performance was tested through a series of esterification reactions using acetic acid as the core reactant. These experiments took place in a 100 mL round-bottom flask equipped with a water-cooled condenser to maintain the reaction environment. To thoroughly evaluate

the catalyst's versatility, the researchers tested it against a diverse library of alcohols, ranging from short-chain methanol to long-chain octanol, and included various structural types such as primary, secondary, tertiary, branched iso-alcohols, and the aromatic benzyl alcohol.

The reactions were carried out under optimized conditions, specifically using a 2:1 molar ratio of acetic acid to alcohol and a consistent catalyst load of 100 mg of SW nanoparticles. The mixture was heated to 110°C in an oil bath and kept under reflux for 2.5 hours. A key part of the strategy involved the choice of solvents: cyclohexane was used for ethyl acetate synthesis, while toluene was employed for all other acetates. These specific solvents were chosen because they form azeotropes with water, allowing the byproduct water to be removed as it formed; this prevented the reaction from reversing and helped drive the yield forward. Finally, the conversion of alcohols into esters was quantified using Gas Chromatography-Mass Spectrometry (GC-MS), with the final percentage yield determined by comparing the amount of ester produced to the starting amount of alcohol.

General reaction scheme for the experiment in Paper 1:

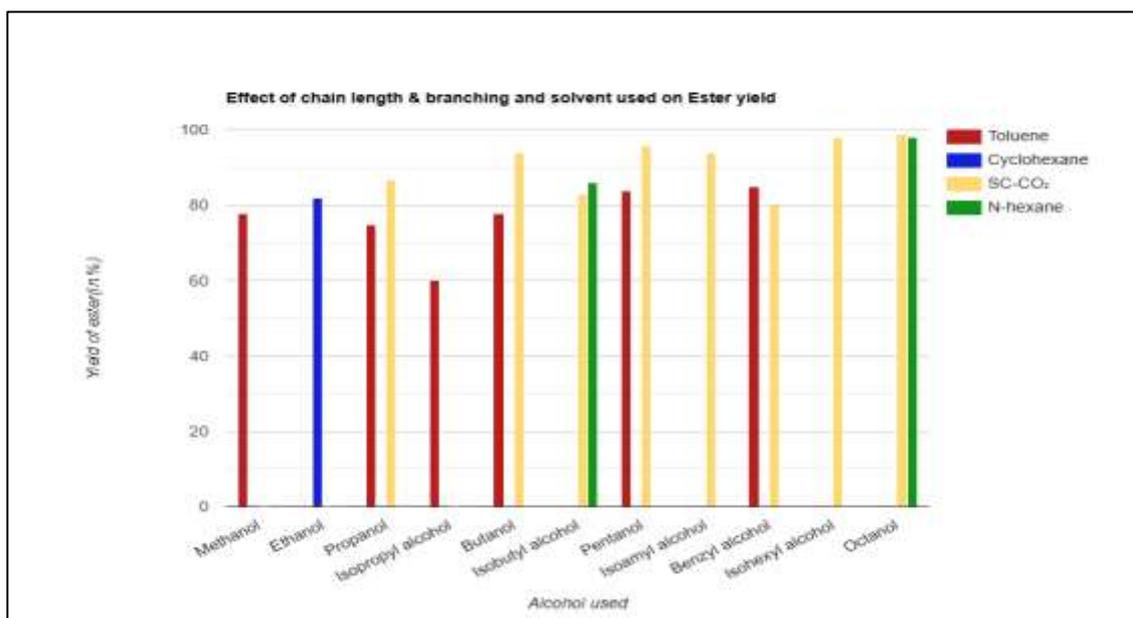


Results

Since paper 2 directly gave results after the **2.5-hour mark** while for paper 1 provided more data with readings till **2 hours**, I will be making a **bar graph** to compare and analyse more accurately between the data. **I will be taking the data at the 120min (2 hour) mark**

from paper 1 as it is the closest to paper 2's data as to make the analysis as precise as possible.

Alcohol used	Paper	Branching present	Degree	Type of solvent used	Yield of Ester(in %)
Methanol	2	No	Primary	Toluene	78
Ethanol	2	No	Primary	Cyclohexane	82
Propanol	2	No	Primary	Toluene	75
Isopropyl alcohol	2	Yes	Primary	Toluene	60
Butanol	2	No	Primary	Toluene	78
2°-Butanol	2	No	Secondary	Toluene	64
3°-Butanol	2	No	Tertiary	Toluene	57
Amyl alcohol(Pentanol)	2	No	Primary	Toluene	84
Benzyl alcohol	2	No(but is an aromatic ring)	Primary	Toluene	85
Propanol	1	No	Primary	SC-CO ₂	87
Butanol	1	No	Primary	SC-CO ₂	94
Pentanol	1	No	Primary	SC-CO ₂	96
Octanol	1	No	Primary	SC-CO ₂	99
Octanol	1	No	Primary	N-hexane	98
Benzyl alcohol	1	No	Primary	SC-CO ₂	80
Isobutyl alcohol	1	Yes	Primary	SC-CO ₂	83
Isobutyl alcohol	1	Yes	Primary	N-hexane	86
Isoamyl alcohol	1	Yes	Primary	SC-CO ₂	94
Isohexyl alcohol	1	Yes	Primary	SC-CO ₂	98



A more focussed bar graph for better visual and easier comparison of the effect of solvent:

Fig 1

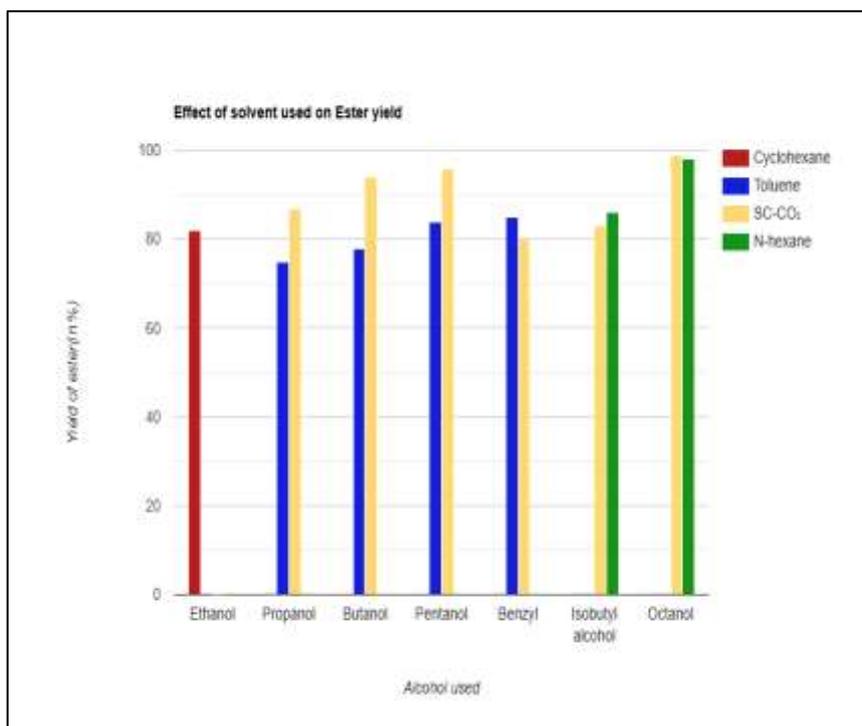


Fig 2

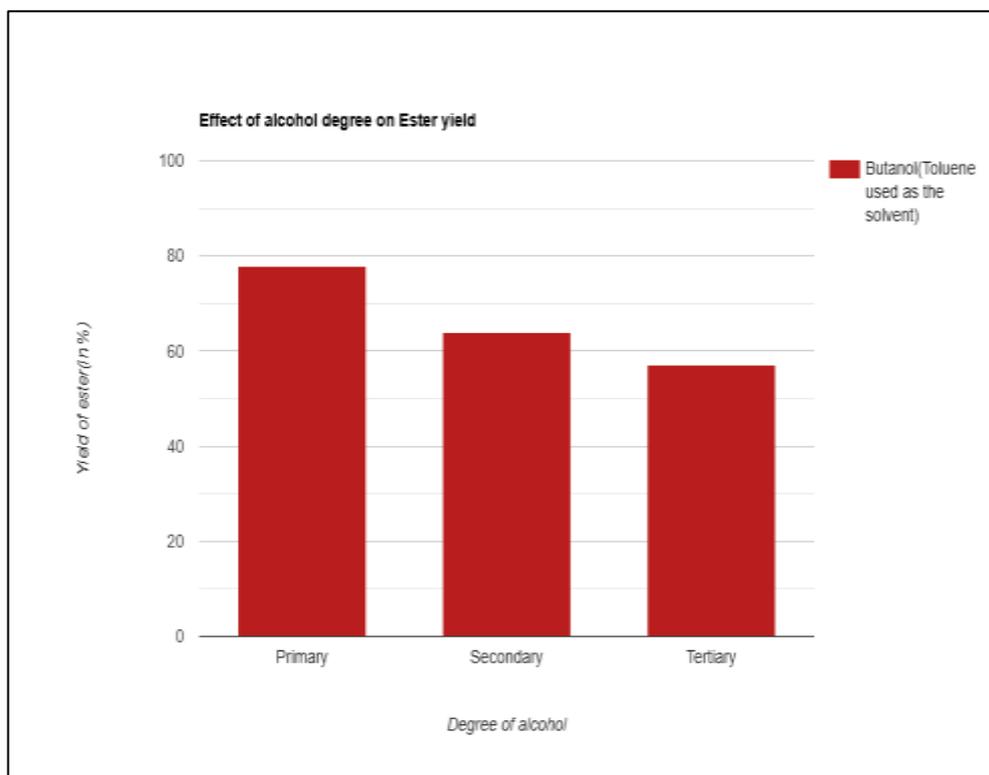


Fig 3

Discussion

The research findings reveal a clear and direct relationship between the molecular structure of alcohols and the resulting ester yield. As the carbon chain length increases from methanol to octanol, there is a consistent rise in productivity, with octanol reaching a near-perfect yield of 99% in SC-CO₂, while methanol remains at the lower end at roughly 78%. A notable exception to this trend is benzyl alcohol; despite its size, its yield is lower than that of pentanol, likely because its bulky aromatic ring creates significant steric hindrance that obstructs the reaction. Branching also plays a detrimental role, typically reducing yields compared to linear counterparts—as seen in the 15% drop between propanol and isopropyl alcohol. Interestingly, this "branching penalty" diminishes in longer chains, perhaps because the bulky groups are further removed from the reactive hydroxyl site. Similarly, the degree of the alcohol shows a strict negative correlation: primary alcohols perform best, followed by secondary, and finally tertiary, where the surrounding carbon atoms physically shield the hydroxyl group from reacting.

Solvent choice proved to be just as critical as the alcohol's structure. Overall, SC-CO₂ emerged as the most effective solvent for most alcohols due to its exceptional diffusivity and ability to dissolve both polar and non-polar components. However, **toluene** outperformed it specifically for benzyl alcohol; since toluene is also an aromatic solvent, it facilitates stronger π - π interactions that improve solubility for aromatic reactants. In other comparisons, **n-hexane** showed an advantage for shorter and branched alcohols due to better non-polar stabilization, while **cyclohexane** appeared more effective than toluene, likely because it lacks the electronic interference of a benzene ring. For large-scale applications, SC-CO₂ and n-hexane appear to be the most viable general-purpose solvents, while toluene remains the specialized choice for aromatic ester synthesis.

It is important to acknowledge certain experimental limitations when comparing these datasets. The two primary studies utilized different control variables that could influence the perceived efficiency. For instance, Paper 1 operated at temperatures between 75°C and 100°C for two hours, while

Paper 2 maintained a higher temperature of 110°C for an additional 30 minutes. Furthermore, the use of two distinct catalysts—the enzyme **Novozyme 435** in one study and **SW nanoparticles** in the other—means that differences in reaction rates and yields could stem from the inherent catalytic activity rather than the solvents or substrates alone.

Conclusion

This research highlights how molecular structure, solvent choice, and catalytic environment collectively dictate the success of esterification. A clear positive correlation exists between alcohol chain length and ester yield, evidenced by octanol's peak performance at 99% in SC-CO₂ compared to methanol's 78% in toluene. However, structural complexity—specifically branching and higher alcohol degrees—introduces steric hindrance that physically restricts access to the reactive hydroxyl group, leading to lower yields. This was particularly evident in tertiary alcohols and aromatic structures like benzyl alcohol. While SC-CO₂ generally served as the superior solvent due to its high diffusivity, toluene proved more effective for aromatic compounds thanks to beneficial π - π interactions. Meanwhile, n-hexane showed advantages for shorter, branched molecules, and cyclohexane outperformed toluene in comparable tests. These nuances suggest that while SC-CO₂ and n-hexane are the most versatile options, solvent selection should be customized based on the specific alcohol used.

The practical implications of these findings are significant for industries ranging from pharmaceuticals to biofuels. Optimizing these parameters allows for more economical and sustainable industrial scaling. Specifically, the success of SC-CO₂ validates it as a "green" alternative that can reduce reliance on toxic organic solvents. Furthermore, understanding how branching and alcohol degrees impact kinetics helps in selecting the most efficient feedstocks for fragrance and flavor production. However, the variations in temperature, duration, and catalysts between existing studies suggest that direct comparisons still harbor potential inaccuracies, emphasizing the need for more standardized research.

To build on this foundation, future experimental work should focus on four key areas:

- **Time Optimization:** Reconciling the 2-hour and 2.5-hour windows used in previous studies to find the ideal reaction duration for different substrates.
- **Controlled Solvent Comparison:** Conducting a single, unified experiment using SC-CO₂, n-hexane, toluene, and cyclohexane under identical conditions to establish a definitive hierarchy of effectiveness.
- **Catalyst Innovation:** Beyond SW nanoparticles and Novozyme 435, exploring new green catalysts could further enhance reaction rates and sustainability.
- **Pressure Dynamics:** Investigating how varying the pressure of SC-CO₂ influences the solubility and reaction kinetics of different ester types.

Bibliography

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