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Overcoming Equilibrium Limitations in Non-Catalyzed Esterification via *In Situ* Water Removal using Molecular Sieves

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Esterification is constrained by its reversible nature, where water accumulation suppresses ester formation and promotes hydrolysis of esters and anhydrides. Although water removal strategies are well established in catalyzed and solvent-based systems, their role in uncatalyzed, solvent-free systems (SFS) remain underexplored. This study investigates the use of molecular sieves (MS) for *in situ* water removal to overcome equilibrium limitations and enhance ester production in a catalyst-free SFS, consistent with green chemistry principles. Batch esterification of isoamyl alcohol with acetic anhydride was conducted using 3 Å and 4 Å MS to examine the effects of adsorbent type, loading (0–10% w/v), temperature (50–80 °C), and reactant molar ratio (2:1–3:1). Incorporation of MS markedly improved yield: without adsorbent, ester concentration reached 2.87 mol/L after 360 min, whereas 6% 3A MS increased yield to 3.81 mol/L (33% enhancement). Reaction acceleration was also evident, with 2.53 mol/L achieved in 75 min using 4% MS compared to 135 min without. While higher temperatures favored ester formation, adsorption efficiency declined above 70 °C. Notably, a 2:1 molar ratio with MS achieved yields comparable to a 3:1 ratio without, demonstrating reduced reliance on excess alcohol. This approach provides a practical, sustainable route to intensify esterification.

Keywords: Green Chemistry, water removal, molecular sieve, solvent-free, non-catalyzed

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Esterification reactions play a vital role in the synthesis of flavors, fragrances, solvents, and bio-based fuels. Isoamyl acetate holds commercial significance due to its strong banana flavor properties leading to an annual demand of 74 tonnes in the USA alone [1]. This demand has been consistently rising over the years where the market is projected to grow by USD 446.4 million from 2024 to 2028, with an estimated compound annual growth rate (CAGR) of 3.3% [2]. The appealing fragrance of isoamyl acetate positions it as a promising candidate for applications in the industry particularly food and flavoring industries.

Despite their industrial relevance, esterification processes are inherently constrained by chemical equilibrium. In such systems, water is often generated as a by-product, and its accumulation can significantly hinder the forward reaction due to equilibrium limitations governed by Le Chatelier's principle [3, 4]. According to Le Chatelier's principle, the accumulation of water shifts the equilibrium back toward the reactants, thereby reducing the overall conversion and yield of the ester product.

To address these constraints, numerous strategies have been developed. Conventional approaches typically rely on acid catalysts and organic solvents to improve reaction rates and conversion efficiency [5, 6]. Additional water removal methods such as azeotropic distillation [7–11], pervaporation, and membrane-assisted processes [12–14] have also been implemented to shift equilibrium toward ester formation. While effective, these techniques introduce drawbacks, including the use of hazardous solvents, increased energy consumption, costly and complex downstream separation requirements.

As a result, attention has shifted toward solvent-free and catalyst-free esterification systems, which align with green chemistry principles. However, these systems remain underexplored due to their stronger susceptibility to equilibrium limitations. One promising route to overcome these challenges is the use of solid adsorbent for *in situ* water removal. Previous studies have demonstrated that molecular sieves (MS) can selectively adsorb water and enhance ester yields in catalyzed or solvent-containing systems [15–24]. Despite these advances, limited to none work has been directed toward water removal in uncatalyzed, solvent-free esterification, where the need to overcome equilibrium barriers is even more pronounced.

Although uncatalyzed esterification generally proceeds at a lower reaction rate compared to catalyzed

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systems, it offers several advantages from both green chemistry and process engineering perspectives. Eliminating catalysts reduces process cost, particularly in systems that would otherwise rely on expensive biocatalysts such as enzymes. In addition, catalyst-free operation removes the need for downstream separation, recovery, and regeneration, simplifying process design and reducing material and energy consumption. Performing the reaction under neat, solvent-free conditions further enhances process simplicity by minimizing additional chemicals and avoiding the use of potentially carcinogenic solvents. This approach aligns with green chemistry principles, including waste prevention and reduced use of hazardous substances, while lowering operational complexity and cost.

The present study addresses this gap by investigating the feasibility of using MS for *in situ* water removal in batch esterification of isoamyl alcohol with acetic anhydride under solvent-free and catalyst-free conditions. The objective of this work is to evaluate the use of MS for selective water removal in uncatalyzed solvent free esterification. Adsorption tests on individual components were conducted to confirm MS selectivity toward water without significant interaction with reactants or product. The effectiveness of *in situ* water removal in overcoming equilibrium limitations was assessed by comparing ester yields with and without MS. In addition, the effects of key process parameters including adsorbent type, loading, temperature, and reactant molar ratio were investigated to determine their influence on ester yield.

EXPERIMENTAL

Chemicals and Materials

All chemicals used in this study were of analytical grade and used without further purification. The chemicals used in this study are summarized in Table 1 together with the respected description, purity, and supplier. The MS were subjected to a pre-treatment activation process prior to use. The activation was conducted by heating the sieves in a muffle furnace at 300–350 °C for four hours. Following thermal activation, the sieves were immediately cooled and stored in an airtight container to prevent moisture re-adsorption. This activation step is done to removes pre-adsorbed water and restore their adsorption capacity, ensuring efficient *in situ* water removal during the esterification reaction. Effective water adsorption by the activated sieves shifts the reaction equilibrium toward ester formation, enhancing overall conversion and yield.

Table 1. List of chemicals used.

Materials/Chemicals	**Description**		**Purity**	**Supplier**
Isoamyl alcohol	Reactants		≥98%	Sigma Aldrich
Acetic anhydride	Reactants		>99%	Thermo Scientific
Isoamyl acetate	GC Standard		≥99%	Merck
Acetic Acid	GC Standard		≥99.7%	Fisher Scientific
Hexane	GC Solvent		≥99.8%	Merck
Ethanol	GC Solvent		≥99.7%	Chemiz
3A MS	**Use**	Adsorbent	-	Sigma Aldrich
	Type	Potassium alumino-silicate $K_nNa_{12n}[(AlO_2)_{12}(SiO_2)_{12}] \cdot xH_2O$		
	Nominal Pore Size	3 Å		
	H_2O Adsorption Capacity	Not stated		
	Size	1.6 mm diameter		
4A MS	**Use**	Adsorbent	-	Sigma Aldrich
	Type	Sodium alumino-silicate $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot xH_2O$		
	Nominal Pore Size	4 Å		
	H_2O Adsorption Capacity	20-25% by weight		
	Size	1.6 mm diameter		

$$\underset{\text{Acetic Anhydride}}{C_4H_6O_3} + \underset{\text{Isoamyl Alcohol}}{C_5H_{12}O_1} \rightarrow \underset{\text{Isoamyl Acetate}}{C_7H_{14}O_2} + \underset{\text{Acetic Acid}}{C_2H_4O_2}$$

[Equation 1]

$$\underset{\text{Acetic Acid}}{C_2H_4O_2} + \underset{\text{Isoamyl Alcohol}}{C_5H_{12}O_1} \leftrightarrow \underset{\text{Isoamyl Acetate}}{C_7H_{14}O_2} + \underset{\text{Water}}{H_2O}$$

[Equation 2]

$$\underset{\text{Acetic Anhydride}}{C_4H_6O_3} + \underset{\text{Isoamyl Alcohol}}{2C_5H_{12}O_1} \leftrightarrow \underset{\text{Isoamyl Acetate}}{2C_7H_{14}O_2} + \underset{\text{Water}}{H_2O}$$

[Equation 3]

Adsorbent and Individual Component Interaction Analysis

This preliminary study evaluated interactions between MS and individual components of the esterification system: isoamyl alcohol, acetic acid, acetic anhydride, isoamyl acetate, and water. Each component (1 mL, 5 mol/L) was prepared in solvent (deionised water in ethanol; others in hexane) and added with 0.4 g MS (40% w/v). Both 3A and 4A MS were tested under ambient conditions (25 ± 2 °C, 250 rpm) for 1 h, with controls run without adsorbent. Concentrations were analyzed to quantify adsorption losses. This screening confirmed MS selectivity toward water and assessed potential interactions with other species prior to esterification experiments. The calculation to quantify percentage of adsorption was calculated using below formula:

$$\text{Adsorption (\%)} = \frac{C_0 - C_t}{C_0} \times 100$$

Where C_0 is the initial concentration of the component (isoamyl acetate, isoamyl alcohol, acetic anhydride, acetic acid, and water), C_t is the concentration of that component after 1 hour of adsorption.

Esterification Reaction

The esterification reaction investigated in this study involves isoamyl alcohol (3-methylbutan-1-ol) and acetic anhydride as the primary reactants. The mechanism of this esterification system involves two main reactions. First, isoamyl alcohol reacts with acetic anhydride to form isoamyl acetate and acetic acid, Equation 1.

Then, the produced acetic acid reacts with remaining isoamyl alcohol to produce additional isoamyl acetate and water, Equation 2.

The overall reaction can be represented as in Equation 3 above [25–27].

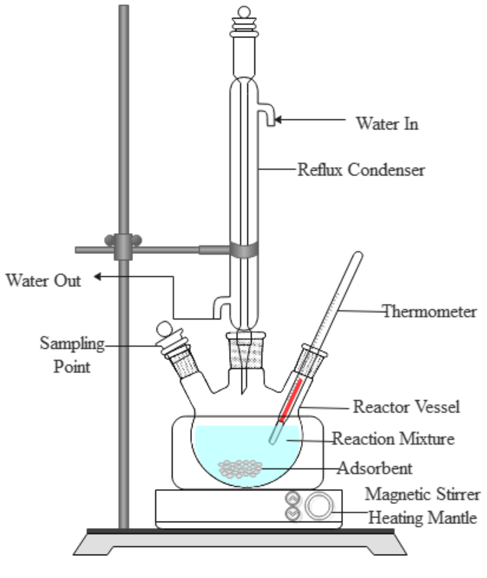

Figure 1. Experiment Setup for Batch Esterification with Adsorbent as Water Removal.

Table 2. Summary of experimental parameters investigated in the water removal of batch esterification between isoamyl alcohol and acetic anhydride.

Parameter	Range/Condition
MS pore size	3 Å and 4 Å
Adsorbent loading	0, 4, 6, 8, 10 (w/v %)
Reaction temperature	50, 60, 70, 80 (°C)
Alcohol-to-acid ratio	2:1 and 3:1, with and without adsorbent

The esterification experiments were conducted in a batch mode using a 100 mL three-neck round-bottom flask, which functioned as the reactor vessel. The flask was fitted with a Liebig condenser to facilitate reflux and to prevent the loss of volatile components during the reaction. A heating and stirring mantle were used to simultaneously regulate the reaction temperature and maintain uniform mixing. Temperature control and monitoring were achieved using a thermometer, which was inserted directly into the reaction medium through one of the necks of the flask. This allowed real-time monitoring and feedback to maintain the desired reaction temperature with minimal fluctuations. A schematic representation of the complete experimental setup is provided in Figure 1.

Isoamyl alcohol and adsorbent (either 3A or 4A MS) was first preheated in the main reactor flask to the target temperature. Simultaneously, acetic anhydride was separately preheated using an auxiliary heating plate. Once both reactants reached the desired temperature, acetic anhydride was introduced into the flask containing isoamyl alcohol. This marked the start of the reaction time, t=0. 100 µL of samples were withdrawn at regular intervals of 15 minutes over a period of 6 hours using a micropipette (IKA PETTE). These samples were subsequently analyzed using gas chromatography.

The effects of several operating parameters were systematically investigated to assess their influence on the esterification yield and water removal efficiency. These parameters are summarized in Table 2. All experiments were performed in triplicate, and the average values are reported.

Analytical Method for Component Quantification

Quantitative analysis of the reaction mixture was performed using gas chromatography with a thermal conductivity detector (GC-TCD, Agilent 7820A, USA) equipped with a WATERCOL™ 1910 capillary column (fused silica, 30 m × 0.25 mm i.d., 0.2 µm film thickness) [28]. Samples (1 µL) were injected manually using a microsyringe. The oven program was optimized to match component volatilities: initial temperature 80 °C; ramped at 20 °C min^{-1} to 100 °C (1 min hold); then to 135 °C (1 min hold); and finally, to 150 °C (1 min hold) to ensure complete elution. The gas and carrier flow rate were fixed at 25.856 mL/min and 10:1. Data were processed with Agilent ChemStation software, and quantification was based on calibration with standard samples. Each run required 7.5 min. Retention times were: isoamyl acetate, 2.0 min; isoamyl alcohol, 2.7 min; water, 3.0 min; acetic anhydride, 3.8 min; and acetic acid, 5.6 min.

RESULTS AND DISCUSSION

Effect of 3A MS and 4A MS on Individual Components

The adsorption behavior of MS with different pore sizes (3 Å and 4 Å) toward individual reaction components provides valuable information into both selectivity and efficiency of water removal in the studied esterification reaction system. As shown in Figure 2, 3A MS exhibited the highest water adsorption efficiency, achieving 76.3% adsorption (from 5.02 mol/L to 1.19 mol/L of water concentration after one hour of contact with MS), whereas 4A MS removed only 20.8% under identical conditions. Both pore sizes (3 Å and 4 Å) are theoretically suitable for water adsorption, given water's kinetic diameter of around 2.75 Å [29–31]. The lower performance of 4A MS is likely due to competitive adsorption of ethanol, the solvent in the system, whose kinetic diameter (4.4 Å) makes it accessible to 4A MS but excluded from 3A MS [32, 33]. This trend agrees with previous findings by Cartón et al. (1987) highlighting the superior selectivity of 3A MS compared to 4A MS in ethanol–water mixtures [34].

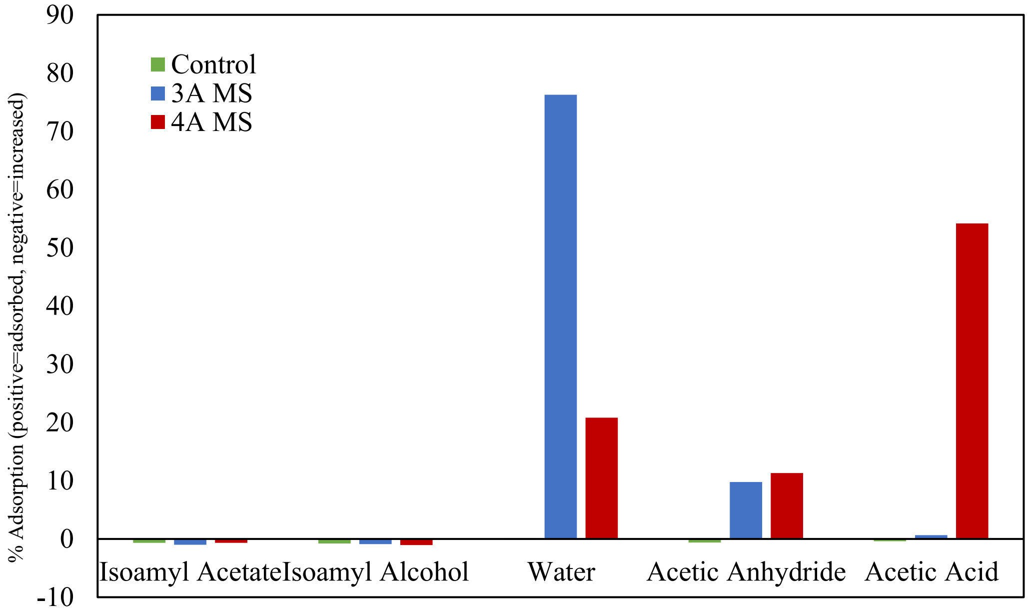

Figure 2. Percentage adsorption of isoamyl acetate, isoamyl alcohol, water, acetic anhydride, and acetic acid by 3A and 4A MS (5 mol/L initial concentration, 0.4 g adsorbent corresponding to 40% w/v, 250 rpm, 25 ± 2 °C, 1 h).

Acetic anhydride showed small percentage adsorption for both MS 3A and MS 4A, 9.75% and 11.3%, respectively. Since no reported kinetic diameter of acetic anhydride is available in the literature, the kinetic diameter, σ, of acetic anhydride was estimated from its critical properties using the correlations proposed as shown in Equation 4 and 5 below [35, 36].

$$\sigma = 0.841 \times \sqrt[3]{V_c} \qquad \textbf{[Equation 4]}$$

$$\sigma = 2.44 \times \sqrt[3]{\frac{T_C}{P_C}} \qquad \textbf{[Equation 5]}$$

V_c is the critical volume in $cm^3\ mol^{-1}$, T_c is the critical temperature in Kelvin and P_c is the critical pressure in atmospheres. Using acetic anhydride data by [37], the estimated kinetic diameter of acetic anhydride is 5.6 Å.

Given this kinetic diameter (kinetic diameter >5 Å), acetic anhydride molecules are too large to diffuse into the micropores of 3A MS or 4A MS, and adsorption through pore is unlikely. However, the adsorption value observed in Figure 2 can be attributed to the susceptibility of acetic anhydride to hydrolysis in the presence of trace water, with the surface hydroxyl groups forming Brønsted acid sites on the MS [38, 39].

Although the molecular sieves were thermally activated at 300–350 °C prior to use, trace amounts of water may still be present due to ambient moisture during handling. Acetic anhydride is highly sensitive to trace amounts of water, as evidenced by multiple studies focusing on its hydrolysis reaction [40, 41]. Therefore, the observed small decrease in acetic anhydride concentration may be due to hydrolysis by residual water in addition to any direct adsorption by the molecular sieves.

Isoamyl alcohol and isoamyl acetate showed negligible adsorption with either sieve. This supports the intended selectivity of MS in this system, as adsorption of reactants or desired product would lower ester yield. In contrast, acetic acid was adsorbed by 4A MS but not by 3A MS, consistent with literature reports that its kinetic diameter (4.4 Å) allows entry into the 4A MS pores [42]. These findings confirm 3A MS as the more effective adsorbent compared to 4A MS for this esterification system, providing high water selectivity with minimal interaction with other components.

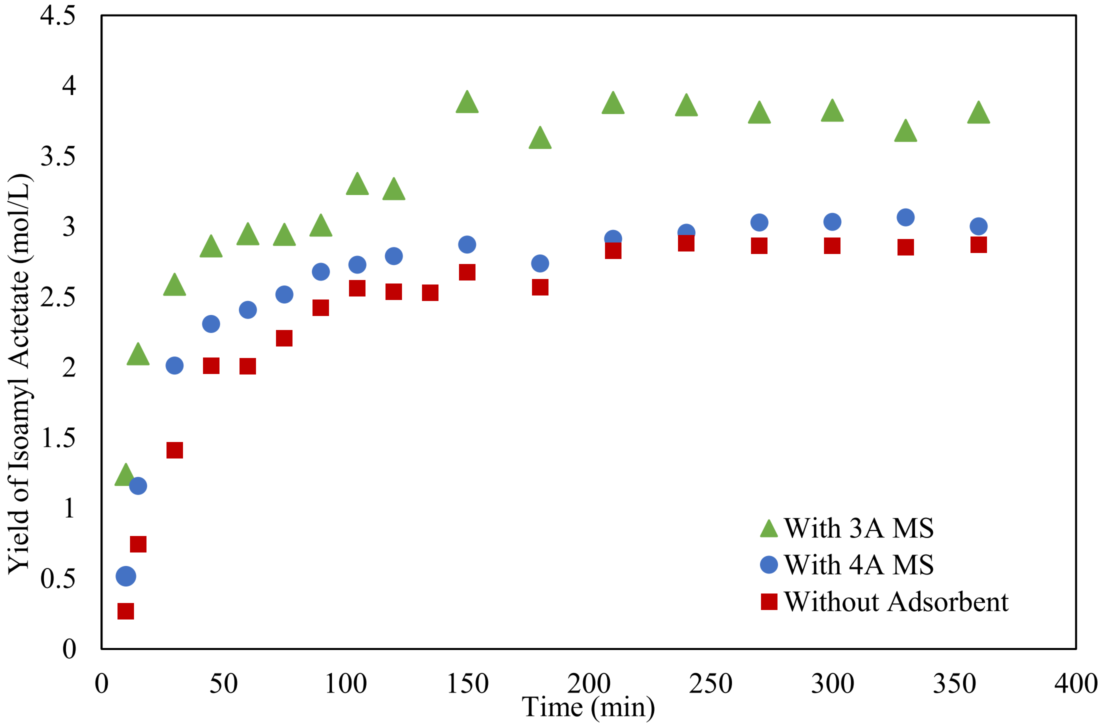

Figure 3. Isoamyl Acetate yield (mol/L) under molar ratio 2:1 (alcohol:acid), 60 °C, with 6% w/v MS loading: without adsorbent (■), with 3A MS (▲), and with 4A MS (●).

Effect of Pore size of MS (3 Å and 4 Å) on Reaction Yield

The effect of pore size of MS on esterification yield provides a clear demonstration of the importance of adsorbent selectivity in equilibrium-limited reactions, that is presented in Figure 3. At 360 minutes, 3A MS produced the highest ester yield of 3.81 mol L^{-1}, compared to 2.87 mol L^{-1} without adsorbent, corresponding to a 33% increase. This improvement arises from efficient water removal, which drives the equilibrium toward ester formation. In contrast, 4A MS achieved only 3.0 mol L^{-1}, a yield nearly identical to the control (without adsorbent), indicating limited effectiveness of 4A MS in promoting conversion. The superior performance of 3A MS aligns with its established selectivity for water over other reaction components, as discussed in Section 3.1. By contrast, the pore size of 4 Å permits the entry of acetic acid, leading to co-adsorption effects that reduce the effective removal of water and consequently lower the esterification driving force [42].

Despite this difference in final yield, both 3A MS and 4A MS exhibited an acceleration of the reaction. For example, at 45 minutes, 4A MS achieved 2.31 mol/L isoamyl acetate, a concentration that the control reaction only achieved around 90 minutes. This early acceleration is consistent with partial water removal at the onset of the reaction. However, as the reaction progressed, competitive adsorption between water and acetic acid reduced the sustained impact of 4A MS. Conversely, 3A MS maintained consistent water selectivity, continuously shifting the equilibrium toward ester formation and delivering the highest final yield.

By excluding molecules larger than water, 3A sieves act as effective equilibrium shifters in esterification system without compromising reactants or products. This emphasizes that adsorbent pore size must be carefully matched to the kinetic diameter of the target by-product to optimize equilibrium-driven esterification process.

Effect of Adsorbent Loading on Reaction Yield

Figure 4 shows that moderate adsorbent loadings significantly enhanced isoamyl acetate formation compared to the control (0% adsorbent, 2.87 mol L^{-1}). At 4% w/v loading, the yield increased to 3.16 mol L^{-1}, further increased to 3.81 mol L^{-1} at 6% and 3.98 mol L^{-1} at 8%. These correspond to improvements of 10%, 33%, and 39%, respectively, relative to the control. The most substantial increase occurred between 4 w/v% and 6 w/v% loading (20 %), whereas the difference between 6 w/v% and 8 w/v% was small (4 %).

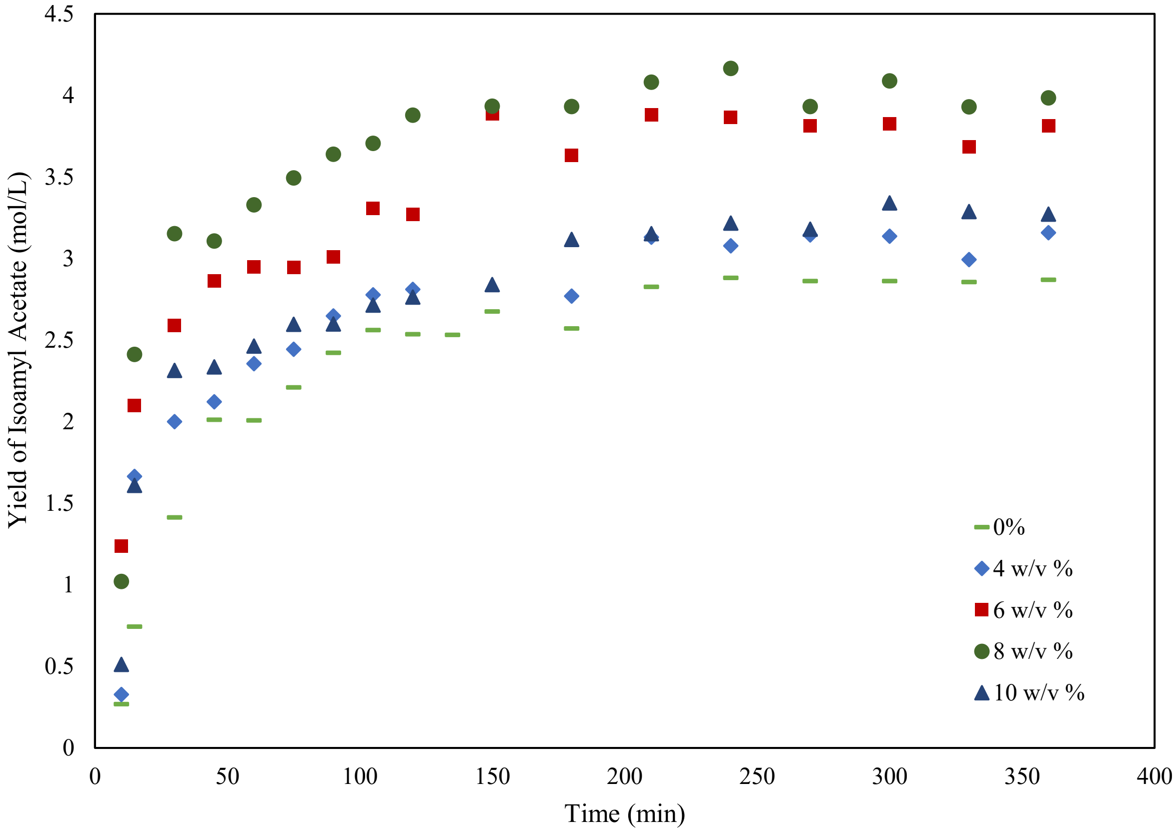

Figure 4. Isoamyl acetate yield (mol/L) as a function of reaction time at 60 °C and 2:1 alcohol-to-acid molar ratio, using 3A MS with different adsorbent loadings (w/v%): 0% (-), 4% (♦), 6% (■), 8% (●), and 10% (▲).

The improvement in yield at increased loadings is attributed to improved water removal capacity, which drives the equilibrium toward ester formation in accordance with Le Chatelier's principle. Higher adsorbent loading provides a greater number of available adsorption sites, enabling faster water removal from the reaction medium [43–45]. Consequently, ester formation proceeds more rapidly. For example, an ester concentration of 2.53 mol L^{-1} was achieved at 135 minutes without adsorbent, whereas the same yield was reached at 75 minutes with 4 w/v% loading. At 6–8 w/v% loadings, the target yield was attained in less than 45 minutes, demonstrating the strong dependence of reaction kinetics on the rate of water removal.

At 10 w/v% loading, the ester yield declined to 3.27 mol L^{-1}, comparable to that obtained at 4%. Excessive adsorbent in the batch system likely induced mass transfer limitations by physically obstructing liquid mixing and reducing effective contact between reactants. Excessive solid adsorbent loading can create a dense fluid that is difficult to agitate, resulting in poor mixing. This limits mass transfer of reactants to the adsorbent surface and consequently reduces the reaction rate [46–48]. This explains the reduction in yield observed at 10% loading despite the greater adsorption capacity.

From a chemical engineering perspective, these observations suggest that while batch systems benefit from moderate adsorbent loading, high adsorbent loading is not favorable due to direct mixing of the adsorbent with the reaction medium [46–48]. A more efficient approach may involve continuous systems, where adsorbent is packed in a fixed-bed or a column separate from the reaction zone, thereby preventing mixing disturbances while maintaining selective water removal.

Effect of Temperature on Reaction Yield

The ester yield profiles with varying reaction temperature are presented in Figure 5. A clear temperature dependence was observed where ester yield increased with temperature from 50 °C (3.15 mol/L) to 70 °C (4.23 mol/L), with small increase at 80 °C (4.44 mol/L).

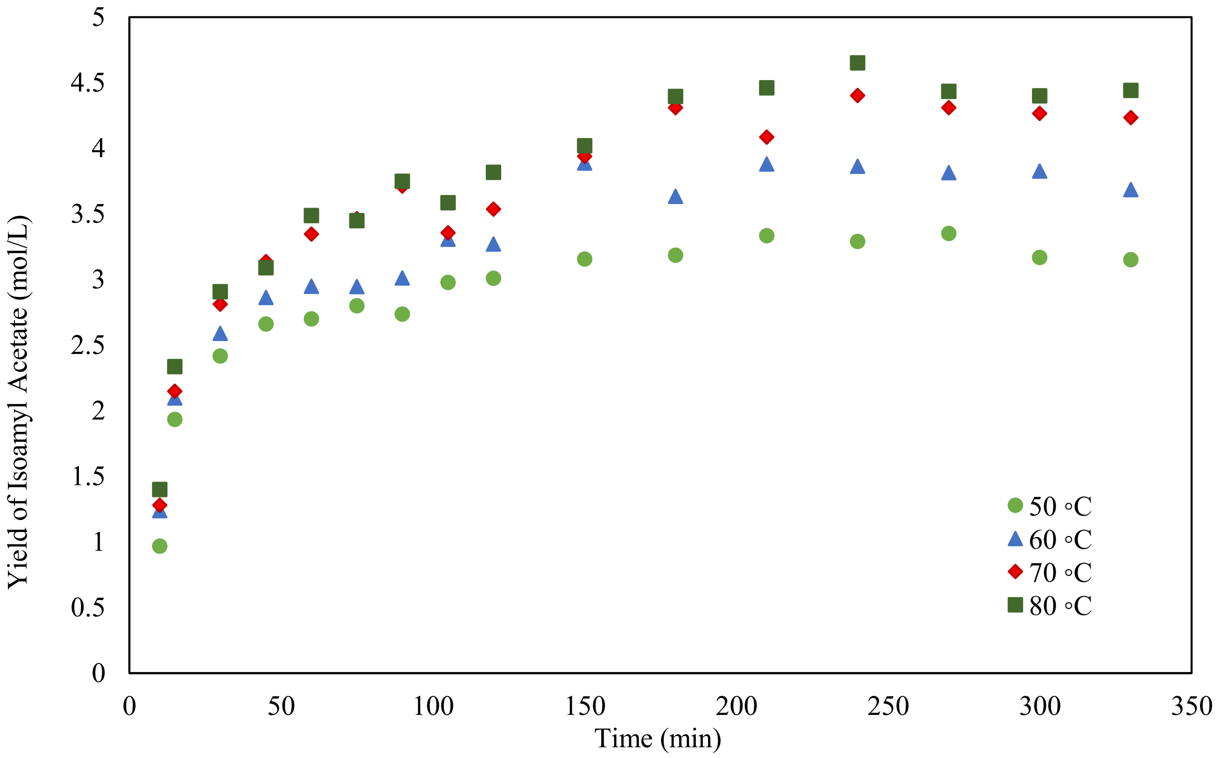

Figure 5. Isoamyl acetate yield (mol/L) as a function of reaction time at different temperatures (50 °C ●, 60 °C ▲, 70 °C ♦, 80 °C ■) under a 2:1 alcohol-to-acid molar ratio with 6% w/v 3A MS loading.

The results demonstrate that high temperature accelerates the reaction kinetics by increasing collision frequency and lowering the activation barrier, thereby enhancing yield [3][44][45]. Similar findings have been reported for esterification reactions, where elevated temperatures significantly improve the forward reaction rate [51, 52].

However, a closer comparison between 70 °C and 80 °C reveals minimal differences in the final yield, with overlapping data points and occasional lower yield at 80 °C. This is due to the temperature-dependent adsorption capacity of the MS [53, 54]. Adsorption of water on 3A MS is an exothermic process, governed by physisorption onto microporous aluminosilicate channels. At lower temperatures, adsorbed water molecules possess insufficient kinetic energy to desorb, resulting in high retention and effective water removal. Conversely, at elevated temperatures, the increased thermal energy enhances desorption, reducing the effective water uptake capacity. This behavior can be rationalized thermodynamically using the van’t Hoff relationship for adsorption equilibrium constants [55].

$$K_{ads} = K_0^{\left(-\frac{\Delta_{ads}H}{RT}\right)} \qquad \textbf{[Equation 6]}$$

where K_{ads} is the equilibrium constant for adsorption, $\Delta_{ads}H$ is the enthalpy of adsorption (negative for exothermic adsorption), R is the gas constant, and T is the absolute temperature. As temperature, T, increases, the exponential term decreases, adsorption constant decreases, indicating reduced affinity of the adsorbent for water. This aligns with prior studies where MS adsorption capacity for polar molecules such as water decreased significantly with increasing temperature.

While higher temperatures accelerate esterification kinetics, they simultaneously reduce the water adsorption efficiency of the sieve. The optimal temperature range is 60–70 °C, where a balance between kinetic enhancement and adsorption efficiency is achieved. At excessively high temperatures, the synergistic benefit of *in situ* water removal is reduced, particularly in batch systems where the adsorbent remains in direct contact with the reaction medium.

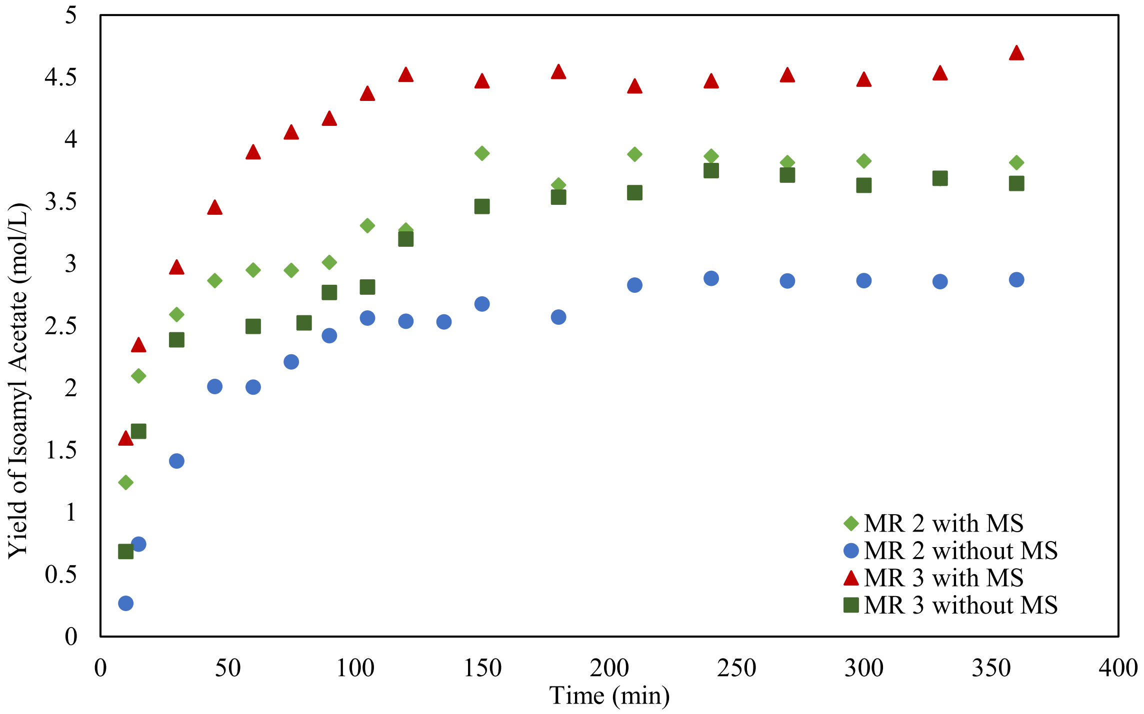

Figure 6. Isoamyl acetate yield (mol/L) as a function of reaction time at 60 °C with 6% w/v 3A MS, comparing different alcohol-to-acid molar ratio(MR): MR 2 with MS (♦), MR 2 without MS (●), MR 3 with MS (▲), and MR 3 without MS (■).

Effect of Molar Ratio on Reaction Yield

Figure 6 shows that increasing the alcohol ratio enhances ester yield, consistent with Le Châtelier's principle, as excess alcohol drives the equilibrium toward ester formation [56–59]. At a 2:1 ratio, the yield reached 3.81 mol L^{-1} with 3A MS, compared to 2.87 mol L^{-1} without adsorbent. Notably, this yield is also comparable to that obtained at a 3:1 ratio without adsorbent (3.64 mol L^{-1}), demonstrating that efficient water removal reduces the need for excess alcohol. The highest yield was achieved at a 3:1 ratio with 3A MS, producing 4.7 mol L^{-1} compared to 3.64 mol L^{-1} without MS, corresponding to an improvement of approximately 28.9 %. These results confirm that both higher molar ratios and selective water removal enhance esterification and minimizes the requirement for large alcohol excess. This observation aligns with Oliveira et al. (2010) that showed in catalyzed and solvent-free esterification, continuous water removal reduces the dependency on excess alcohol, lowering separation costs and simplifying downstream processing [60]. For industrial applications, this is particularly advantageous, as minimizing alcohol excess not only lowers recovery costs but also improves overall process efficiency.

CONCLUSION

In-situ water removal using MS is feasible and an effective strategy to overcome equilibrium limitations in solvent-free and uncatalyzed esterification. The batch esterification of isoamyl alcohol with acetic anhydride revealed that 3A MS selectively removed water, leading to substantial improvements in yield while maintaining minimal interaction with reactants and products. At 6% adsorbent loading, the ester concentration increased by 33% compared to the no-adsorbent case, and comparable yields were achieved in less than half the time, confirming the kinetic and benefits of continuous water removal. Parametric studies further established that adsorbent loading, temperature, and molar ratio significantly influence reaction performance. Optimal MS loading was identified at 6–8 w/v%, with higher values leading to mass transfer limitations. Elevated temperatures enhanced product yield but reduced adsorption efficiency, resulting in negligible yield differences between 70 and 80 °C. Variation of molar ratio showed that excess alcohol improved ester formation. Furthermore, a 2:1 ratio with 3A MS achieved yields comparable to a 3:1 ratio without, underscoring the potential to reduce alcohol usage and lower process costs. This research provides the first demonstration that selective water removal using MS can drive solvent-free, uncatalyzed esterification toward higher yields. By combining green chemistry principles with process intensification, this approach offers a practical and sustainable pathway for ester production without the need for catalysts or solvents, paving the way for more cost-efficient and environmentally friendly industrial applications.

OUTLOOK

This study has shown the potential of using adsorbents for selective water removal in solvent-free and uncatalyzed esterification batch system. Building on these findings, several important directions for future research should be considered to further evaluate and establish the applicability of this approach. First and foremost, the methodology should be extended to a wider range of esterification systems. Investigating other ester systems experimentally would help validate the general applicability of adsorbent-based water removal in solvent-free and uncatalyzed systems.

Moreover, while the use of adsorbents can clearly enhance ester yield and reduce downstream separation requirements, the economic feasibility of this approach remains insufficiently addressed. It is important to assess whether the improvements in product yield justify the cost of applying adsorbent including the energy required for regeneration. Comparative techno-economic analysis (TEA) is needed to quantify these trade-offs and evaluate the cost-benefit ratio in contrast to conventional separation methods.

Alongside economic considerations, environmental sustainability must also be evaluated through life cycle assessment (LCA). This includes examining the impacts of raw material sourcing, adsorbent longevity, energy consumption, and disposal at end-of-life. Together, TEA and LCA frameworks will be essential in positioning adsorbent-based systems as both technically and environmentally viable, in alignment with the principles of green chemistry and sustainable process development.

Moreover, it is essential to investigate the application of this strategy in continuous systems. While batch systems offer simplicity and control, continuous operation better reflects industrial practice. Implementing adsorbents in flow systems introduces new challenges, including maintaining uniform flow distribution, preventing pressure build-up, and ensuring consistent adsorbent performance over extended periods. Addressing these challenges through system design and process optimization will be critical for enabling real-time, intensified esterification processes with integrated water removal.

Future work that addresses this research directions will help transform adsorbent-assisted water removal from a laboratory concept into a practical and scalable solution for industrial esterification and other water-sensitive chemical reactions processes.

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