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Sustainable Synthesis of Di-iso-octyl Maleate Using 3-octanol Extracted from Peppermint Oil

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Abstract
Surfactants are vital in industries such as detergents, textiles, and cosmetics, and their synthesis from renewable or waste-derived feedstocks aligns with sustainability goals. This study explores the valorization of 3-octanol, a byproduct of peppermint oil extraction, into di-isooctyl maleate (DOM), a precursor to di-octyl sulphosuccinate (DOSS), a widely used surfactant. The synthesis of DOM was achieved via esterification of 3-octanol and maleic anhydride in the presence of para-toluene sulphonic acid (PTSA) as a catalyst. Reaction parameters, including catalyst concentration, reaction time, and temperature, were systematically optimized to maximize yield. The highest yield of 96.34% was obtained using 0.4 g of PTSA per 5 g of 3-octanol, with an optimal temperature of 80–85°C and a reaction time of 3 hours. Experimental data showed a decline in yield beyond this catalyst concentration and reaction duration, indicating the importance of precise parameter control. Alternate catalysts such as Amberlite and Indion 130 were tested. This study demonstrates a sustainable and scalable approach to converting waste-derived 3-octanol into value-added surfactants, providing an economically viable solution with minimal equipment and investment requirements.

Keywords: Peppermint oil, 3-Octanol, Esterification, Waste valorization, Renewable feedstock, Sustainable surfactant synthesis.

1. Introduction

Surfactants are chemicals that reduce the interfacial tension between two immiscible liquids, or between liquids and gases, or liquids and solids. The chemical composition of most surfactants includes a hydrophilic head and a hydrophobic tail. Based on the charge on the hydrophilic residues of the surfactant molecule, surfactants are classified as anionic, cationic, and non-ionic, having negatively, positively, and neutral charged ions, respectively. Surfactants are most widely used in detergents and cleaning agents for domestic and industrial applications. The most common surface-active chemical group in detergents is alkylbenzene sulphonates (1). Surfactants are also widely applied as emulsifiers. Mild surfactants are used in skincare and body products. Examples of these surfactants are ether sulphates, ether carboxylates, and sulfosuccinate esters, which are derived from fatty alcohol polyglycol ethers (1). The textile industry is another sector where surfactants are widely used. For washing wool, mostly non-ionic surfactants are employed, while cotton requires both non-ionic and anionic surfactants (1). Bis(2-ethylhexyl) sulphosuccinate, more commonly known as 'Docusate' or Dioctyl sodium sulphosuccinate (DOSS), is an anionic surfactant with a wide variety of applications. One important application of DOSS is as a stool softener to treat chronic constipation (2). Docusate is also used as an adjuvant in some classes of pesticides (3). The anionic salts of Docusate, when combined with organic counter-ions, can modify the surface parameters of usable liquids and form ionic liquids (3). The market for Di-Octyl Sulphosuccinate in 2023 was valued at $460 million, with a projected CAGR of 5.9% from 2024 to 2030. The largest share of DOSS was in the paints and coatings industry, followed by surfactants and textiles at the second and third positions, respectively (4). All analyses show that the market for Di-Octyl Sulphosuccinates will grow steadily over the next 8–10 years (4). Major players in the manufacturing of surfactants include Colonial Chemicals Inc., Croda International PLC, EOC Group, Galaxy Surfactants, Huntsman Corporation, JLK Corporation, and The Dow Chemical Group, among others (5). The alcohol used in this experiment is 3-octanol, a byproduct of peppermint oil extraction (6). After the extraction process is complete, the percentage of 3-octanol ranges from a minimum value of 0.3% to a maximum value of 0.5% (wt%) (7). The synthesis of Di-Octyl Sulphosuccinate is a two-step process. The first step involves the formation of an ester (di-isooctyl maleate) by the reaction of one molecule of maleic anhydride with two molecules of octanol or an isomer of octanol in the presence of para-toluene sulphonic acid as the catalyst. The second step is the formation of the succinate from the previously formed ester through sulphonation, via reaction with sodium metabisulphite, with ethanol as the solvent under reflux (8).

2. Experimental

3-Octanol was obtained by extraction from peppermint oil. Maleic anhydride, toluene, and para-toluene sulfonic acid were purchased from SD Fine Chemicals. The progress of the reaction was monitored using thin-layer chromatography (TLC).

Synthesis of Di-isooctyl Maleate (DOM)

The synthesis of DOM involves the reaction of maleic anhydride (1.88 g) with 3-octanol (5 g) under normal atmospheric conditions at a temperature range of 80–85°C for 3 hours with vigorous stirring. Toluene was used as a solvent, and para-toluene sulfonic acid (0.4 g) was used as the catalyst. The progress of the reaction was monitored using TLC. After 3 hours, the catalyst was separated by filtration, and the excess toluene was evaporated for 2 hours at 100°C under normal atmospheric conditions. The resulting reddish-brown and clear solution was collected as the final product, DOM, which was characterized by GC-MS.

3. Results and Discussion:

The experiments conducted in this study focus only on the first step of the synthesis of DOSS, which is the synthesis of DOM. The conversion of the specific waste stream of 3-octanol to di-octyl maleate represents a waste valorization approach, using maleic anhydride as the reactant and para-toluene sulfonic acid as the catalyst. Aromatic sulfonic acids, such as para-toluene sulfonic acid, are synthesized from sulfuric acid (H_2SO_4) and are strong acids (9). Para-toluene sulfonic acid is widely used as a catalyst for the conversion of biomass into value-added products. For example, PTSA can be employed in the production of levulinic acid from cellulosic biomass (10). Processes involving conventional liquid acids face several challenges, such as equipment corrosion, hazardous reaction mixtures, and difficulties in separation and purification. Solid catalysts offer a better alternative to liquid catalysts, providing improved yields and better operating conditions. PTSA is a crystalline solid, typically white in color, and is soluble in water, alcohols, and other organic solvents. Para-toluene sulfonic acid is a strong, non-oxidizing acid (11). In this paper, the effects of various parameters such as temperature, reaction time, and the amount of catalyst used in the reaction are studied. The weight of the catalyst was varied from

0.1 to 0.5 g. For each batch, 6 mL (or 5 g) of octanol was combined with 1.88 g of maleic anhydride. The molar ratios of catalyst to octanol for each case are as follows:

Batch No.	Wt. of Catalyst (gm)	Moles of catalyst/ moles of octanol	Yield (%) (w.r.t Di-octyl Maleate)
1	0.1	0.01514	62.29
2	0.2	0.0303	81.33
3	0.4	0.0606	96.34
4	0.5	0.0757	95.48

Table. 1: Comparison of molar ratio of catalyst to raw material to the yield of the batch

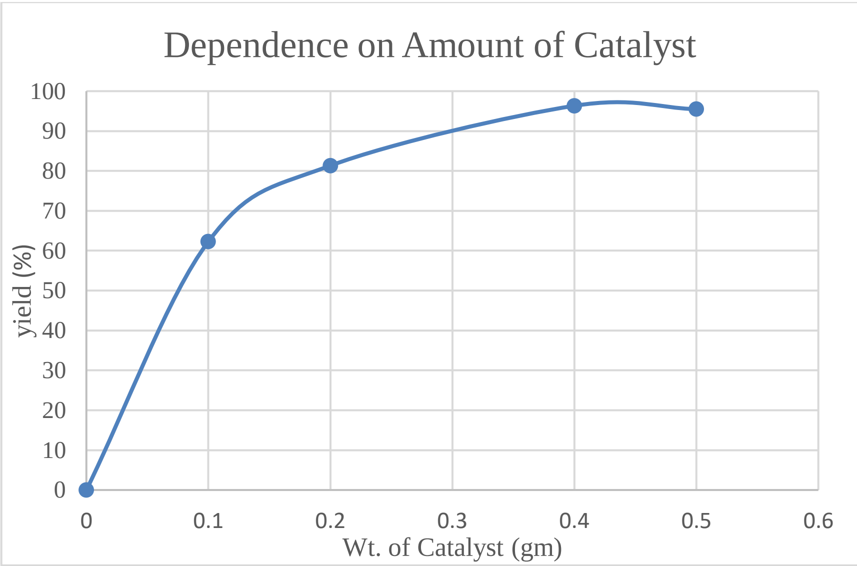

Fig. 1: Graph of weight of catalyst to the yield of the batch reaction

When the amount of catalyst was increased to 0.4 grams, the yield of DOM reached 96.34%. However, it can be concluded that the maximum yield is achieved with 0.4 grams of PTSA for 5 grams of 3-octanol, and further increases in catalyst amount do not improve the yield. When the reaction time was increased from 2 hours to 4 hours, the yield of the reaction increased to 91.9%. Upon further analysis, the maximum yield was determined to be 92.55%. Therefore, it can be concluded that the maximum yield is achieved between 4 and 5 hours.

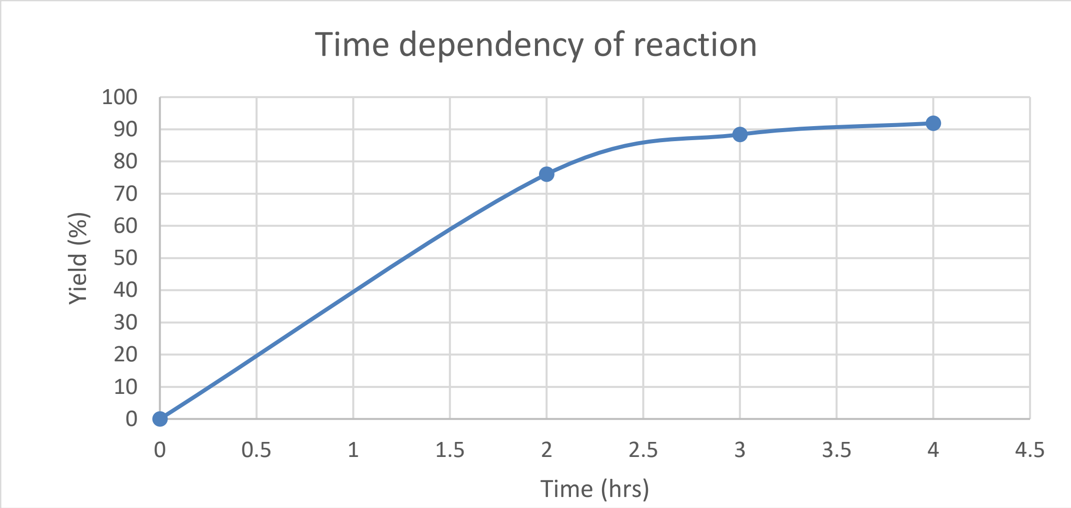

Fig. 2: Graph of increasing time versus the yield at 80-85^{o}C of subsequent batches

The reaction temperature was varied from 75°C to 97°C. It was observed that there is an optimum temperature range within which the desired product is formed. In this case, temperatures exceeding 103°C caused the reaction mixture to turn reddish-black. Therefore, the reaction temperature was maintained below 100°C.

Fig. 3: Colour of reaction mixture at 102.3^{o}C

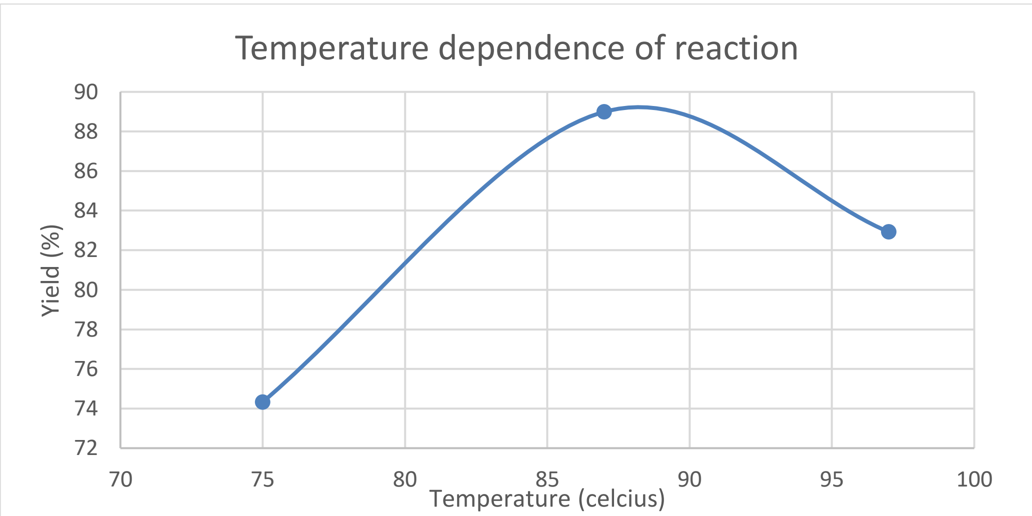

Fig. 4: Graph of temperature of reaction versus yield of reaction for 3 hours of subsequent batches

When the mathematical relationship of the data was analyzed, the maximum yield was estimated to occur at 88.36°C. Amberlite and Indion 130 catalysts were also tested as alternative catalysts for the synthesis. TLC was performed to verify the formation of DOM in the reaction mixture. Each reaction was conducted at 80–85°C until completion.

4. Conclusion:

3-octanol was successfully valorized through its conversion into a textile-grade surfactant. The chosen process is cost-effective, scalable. Key parameters such as catalyst type, reaction time, temperature, and the molar ratio of catalyst to raw material were thoroughly examined and optimized. PTSA, a sulphonic acid catalyst, was utilized in both stages of the surfactant synthesis process.

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