

Influence of Process Conditions on Glycerol Esterification Catalyzed by Tetra-N-Butylammonium-Modified Montmorillonite Catalyst

Iman Hashemizadeh, Ahmad Zuhairi Abdullah

School of Chemical Engineering, University Sains Malaysia, Engineering Campus, 14300 Nibong Tebal, Penang, Malaysia.

chzuhairi@eng.usm.my

Abstract - Selective synthesis of glycerol monolaurate from glycerol and lauric acid was investigated. Loading of tetra-n-butylammonium modified montmorillonite catalyst (1-5 wt. %), reaction temperature (110-140 °C) and glycerol to lauric acid ratio (4:1 to 8:1) were used as variables and the performance was based on lauric acid conversion and glycerol monolaurate yield. Geometrical constraint in the pores retarded the formation of higher glycerides. Increasing catalyst loading improved the monolaurate yield. Fast reaction occurred within the first 8 h and 3 wt. % was deemed the optimum catalyst loading. No further benefit was achieved above 130 °C and 6:1 for the reactant ratio. Impressive lauric acid conversion of about 80 % with corresponding glycerol monolaurate yield of 70 % were achieved in 8 h at 130 °C, using a reactant ratio 6:1 and 3 wt. % of catalyst. The modified montmorillonite was therefore active and highly selective for the production of monolaurate.

Key words: Esterification ; Monolaurate, montmorillonite, tetra-n-butylammonium; selectivity.

Introduction

The development and commercial use of biodiesel has been rapidly expanding over the last 10 years. In biodiesel production process, glycerol is produced at a rate of about 10 wt. % of total biodiesel produced and presently, its production creates a glut in the market (Bossaert et al., 1996). It plays a very important role as a major by-product toward the price trend of biodiesel (Abdullah et al., 2007). Several factors including its low price, availability and functionality make glycerol very attractive for many industrial processes. Glycerol is expected to become a major chemical platform for future biorefineries since it has emerged as an important organic building block (Hermida et al., 2011). As such, research attempts for the conversion of glycerol into value-added substances seem to worthwhile efforts.

Monoglycerides or more correctly known as monoacylglycerols, are glycerides consisting of one fatty acid chain covalently bonded to a glycerol molecule through an ester linkage. Monoglycerides consist of a hydrophilic head and a hydrophobic tail, which give them detergency characteristics. Therefore, monoglycerides and their derivatives have a wide application as emulsifiers in food, pharmaceutical and cosmetic industries (McClements, 2005 ; Bossaert et al., 1996). The global production of emulsifier is estimated at approximately 200,000-250,000 metric tons per year (Moonen and Bas, 2004) and expected to further increase in the future. These substances have various applications in different fields such as in cosmetics, pharmaceutical formulations, drug delivery systems, oil well drilling, textile, packaging, plastic processing and construction materials (Hermida et al., 2011). The conversion of glycerol to monoglycerides could provide interesting solution to improve the overall economy of biodiesel industry worldwide.

There are two major industrial routes to produce monoglycerides. They are usually manufactured through glycerolysis, a base-catalyzed transesterification of triglycerides with glycerol at elevated temperature. Secondly, monoglycerides may be produced through a direct, single esterification of glycerol with fatty acids catalyzed by acids (Wilson et al., 2000). As the three hydroxyl groups in glycerol do not strongly differ in reactivity, the current industrial processes for mono ester production both lead to mixtures of mono- (40-60 %), di- (35-45 %), and even triglycerides (Gupta, 1996). Techniques for purification of monoglycerides are expensive and involve the use of high temperature leading to the development of unwanted flavors and side products. Therefore, it is highly desirable to improve the monoester yield by choosing favorable reaction conditions and designing an appropriate selective solid catalyst.

Solid catalysts are reported to be sufficiently active catalysts for esterification of fatty acid with glycerol (Bossaert et al., 1999 ; Hermida et al., 2011). However, active catalysts could also promote the formation of di- and triglycerides to result in poor selectivity to monoglyceride. As such, solutions to selective monoglyceride production could stem from unique pore characteristics of the catalyst to consequently allow shape selective catalysis. Recently, there has been considerable interest to use clays to catalyze organic reactions (Bokade and Yadav, 2009). Montmorillonite, a natural smectite, has been found to be a useful catalyst in a variety of organic reactions due to its strong acidity, inexpensive compared to ion exchange resin, noncorrosive, reusability and non-polluting (Bahulayan et al., 2003 ; Abdullah et al., 2011). Reactions catalyzed by montmorillonite clays are usually carried out at relatively mild conditions with high yield and selectivity towards the desired products (Abdullah et al., 2011).

The use of montmorillonite in conjunction with phase transfer catalyst (PTC) provides potential synergical effects of their properties and catalytic activity. When mixed with organic molecules, this clay mineral presents a proton rich environment to theoretically affect the reaction. On the other hand, the catalytic abilities can also be improved by incorporating the organic cations in the interlamellar space which enables better accessibility of reactants. This study addresses the behavioral study of tetra-n-butyl ammonium montmorillonite in catalyzing selective synthesis of glycerol monolaurate from glycerol and lauric acid.

Materials and Methods

Materials

Na-montmorillonite (Na-MMT) clay with a cation exchange capacity (CEC) of 119 meq/100 g was supplied by Kunimine Industry Co., Japan. The surfactant used in this study was tetra-n-butylammonium bromide (TBAB, $C_{16}H_{36}BrN$, FW: 322.368) from Sigma Aldrich. Lauric acid (Fisher) and glycerol (Fisher) with a purity of 99% were used without further purification.

Catalyst Preparation and Characterization

A method as reported by He et al. (2009) and Wibowo et al. (2009) was used to prepare the modified clay catalyst. A stoichiometric amount of TBAB was first dispersed in 400 mL of distilled water at 80 °C under stirring at about 600 rpm. Then, 5.0 g of Na-MMT which was pre-dried at 105 °C for 1 h was added slowly and the stirring was continued for another 3 h. The organoclay product was then thoroughly washed until it was completely free of bromide anions as determined by the use of $AgNO_3$. It was then dried at room temperature, ground in an agate mortar, screened with a 200-mesh sieve and stored in a dry cabinet before use. The parent (NaMMT) and the modified montmorillonite catalyst (TBMMT) were characterized using XRD and surface analysis methods by means of a Siemens 2000X system and Micromeritics ASAP 2020 systems, respectively.

Esterification of Glycerol with Fatty Acid

The esterification of glycerol with lauric acid was performed in a 250 mL stirred flask heated in an oil bath under atmospheric pressure. Variable amounts of catalyst between 1 wt. % to 5 wt. %, previously dried at 100 °C overnight were used in a reaction temperature range of between 110 °C and 140 °C for up to 12 h. The lauric acid to glycerol molar ratio was varied between 4:1 and 8:1. For product analysis, samples from the reaction vessel were withdrawn at various intervals to be analyzed for their composition. For the analysis of the product mixture, 100 μ L of the sample withdrawn from reaction vessel was first added into 100 μ L of water and 100 μ L of methyl acetate. The solution was then vortexed and the organic phase containing acylglycerols and fatty acid was separated by means of centrifugation. The composition was then analyzed using a Hewlett Packard HP 5800 gas chromatograph equipped with an FID.

Results and discussion

Characteristics of the Catalyst

The calculated basal spacing from the Bragg equation and the results of surface analysis on the catalysts are shown in Table 1. The basal spacing was found to increase from 1.1 to 1.7 nm when the TBAB was intercalated into the parent montmorillonite. The basal spacing of montmorillonite could reach about 2.0 nm was reported when a larger molecule octadecyltrimethylammonium bromide ($C_{21}H_{46}NBr$) was exchanged into montmorillonite (Xi et al., 2004). As such, changes in the basal spacing could be influenced by the size of intercalated molecules in the clay inter layers.

Table 1. Basal spacing and surface characteristics of NaMMT and TBMMT.

Sample	Basal spacing (nm)	S_{BET} (m^2/g)	d_{pore} (nm)	V_{pore} (cm^3/g)
NaMMT	1.1	24	4.1	0.04
TBMMT	1.7	11	14.0	0.05

Significant enlargement of basal spacing could be of significant contribution when dealing with catalytic conversions involving large molecules such as fatty acid. Surface analysis showed that clay was a low surface area material with a surface area of 24 m^2/g and the mean pore size was in mesoporous size range. As theoretically expected, the exchange of native sodium ions with the surfactants resulted in significant drops in the surface area and correspondingly, significant enlargement of the pores occurred. The effect on the pore diameter was indeed consistent with the basal spacing increase as noted in the XRD results.

Effect of Catalyst Loading

The variations in lauric acid conversion and monoglyceride yield were demonstrated by keeping other variables constant in order to study the effects of catalyst loading on the esterification process. As noted in Figures 1(a), significant conversions took place without the use of any catalyst. This was attributed to autocatalysis by lauric acid which acted as a

catalyst besides being a reactant. However, the use of TBMMT clearly improved the glycerol monolaurate yield, suggesting some degree of shape-selective catalysis might have taken place. This was attributed to the higher number of active sites and pore characteristics to suppress the formation of by-products.

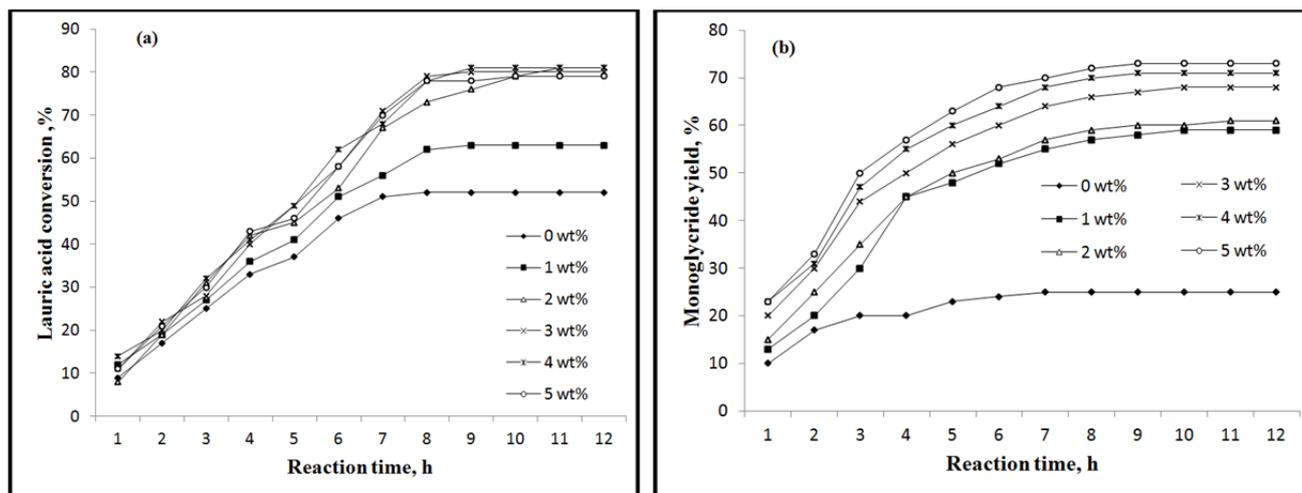


Figure 1. Effect of various catalyst loadings on a) lauric acid conversion and b) monoglyceride yield in the glycerol esterification with lauric acid (Glycerol:lauric acid molar ratio 6:1, 130 °C).

After relatively sharp increases in the first 8 h, the conversions leveled off for all catalyst loadings. Therefore, the reaction reached its equilibrium after about 8 h due to low reactant concentration and high concentration of products to shift the equilibrium towards the reactants side. The reaction time to reach equilibrium was not significantly influenced by the catalyst amount. However, increasing catalyst loading clearly resulted in higher conversion until about 3 wt. %. At higher loading, liquid phenomena between the glycerol and lauric acid which are mutually immiscible could play significant role in controlling the overall rate of reaction. Similar behavior was reported by Hermida et al. (2011) in a similar catalytic system using an acid functionalized SBA-15 catalyst.

Without the use of the catalyst, the monoglyceride yield reached in the esterification was only about 25 % and it was due to the co-formation of di- and triglyceride in the homogeneous reaction. This observation clearly showed the disadvantage of the homogeneous system. In the presence of a solid catalyst, the formation of di- and triglyceride with significantly larger molecule sizes was retarded due to geometric constraint in the catalyst pores. As such, the formation of monoglyceride was favored to give better yield. However, the formation of higher glycerides was still possible at larger pores, especially those at the interstices between catalyst particles. Unlike the trend in the lauric acid conversion, increasing catalyst loading to 5 wt. % led to a gradual increase in the yield.

Bossaert et al. (1999) comparatively studied the effect of variable loading of MCM-41-SO₃H and SBA-15-SO₃H catalysts between 0 and 5 % in the synthesis of monoglyceride performed under similar reaction conditions. Similar to this result, they observed a monotonous increase of the conversion and monoglyceride yield to imply that transfer of reactants from one liquid phase to another was not rate-limiting. This observation suggested the higher catalytic activity of TBMMT compared to those MCM-41-SO₃H and SBA-15-SO₃H. This conclusion was based on the effect that the overall reaction rate is governed by the rate-limiting step (Bokade and Yadav, 2009).

Effect of Reaction Temperature

Figures 2(a) and 2(b) respectively illustrate the enhancement observed in lauric acid conversion and monoglyceride yield in the reaction carried out at 4 different temperature increase in the reaction temperature. At a temperature of 110 °C, the lauric acid reached a plateau after 5 h of reaction which could be attributed to a shift in the reaction direction. This observation led to a conclusion that the equilibrium in this reaction was influenced by the reaction temperature.

In order to carry out the esterification reaction to completion, appropriate temperature with efficient removal of water was required as water (by-product) could promote the reverse reaction. Monoglyceride yield of 70 % with corresponding lauric acid conversion of 80 % was achieved in 8 h at 130 °C. Higher temperature neither significantly improve the conversion nor the yield. It could be explained on the basis of increasing mass transfer of the fatty phase with the increase in temperature. As the reaction generally occurs in the fatty phase, glycerol molecules have to be transferred into this phase prior to the reaction. Then, glycerides (mono-, di- and triglyceride) were formed and an increase in the lauric acid conversion was observed (Wilson et al., 2000).

No significant improvement in the fatty acid conversion and glycerol monolaurate yield was observed by increasing the temperature beyond 130 °C. At lower temperatures, more reaction took place with increasing temperature as the system was kinetic-controlling. However, when the reaction was sufficiently fast at 140 °C, liquid phenomena such as diffusion rate of fatty acid in the excess glycerol could have compensated the beneficial effects of higher reaction temperature.

Sanchez et al. (1997), Bossaert (1999), Diaz et al. (2001) and Machado et al. (2000) investigated temperature effects in direct esterification of glycerol by fatty acid. The range of reaction temperature studied was 90–160 °C. At high fatty acid conversions, the selectivity to monoglycerides decreased due to the production of diglycerides and also triglyceride on the external surface of the catalyst. In this respect, TBMMT catalyst used in this study offered a particular advantage as

corresponding increase in the yield with increasing fatty acid conversion was obtained. The interlayer spacing within meso size range was deemed the responsible factor to the suppression of di- and triglyceride formations.

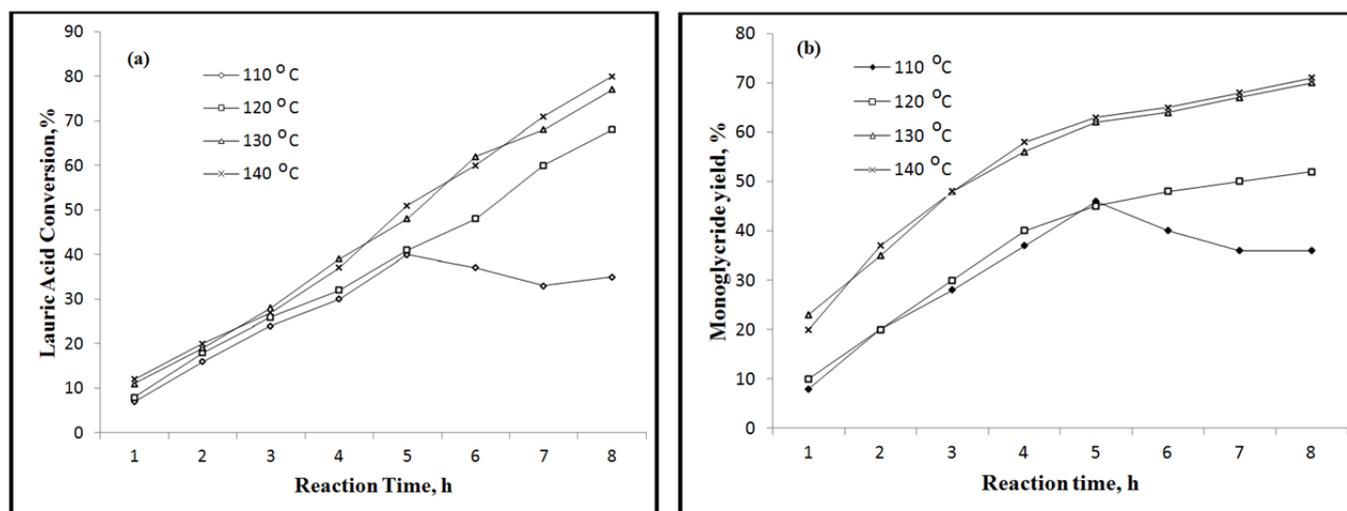


Figure 2. Effect of reaction temperature on a) lauric acid conversion and b) monoglyceride yield in the glycerol esterification reaction. (Glycerol:lauric acid molar ratio 6:1, catalyst loading 3 wt. %).

Effect of Glycerol/lauric Acid Molar Ratio

Esterification of glycerol with fatty acid to produce monoglyceride is a reversible reaction. Based on stoichiometry, the esterification reaction requires glycerol/fatty acid molar ratio of 1:1 to produce monoglyceride. In reality, di- and triglyceride could also form in the reaction so that excess glycerol is needed. In order to investigate the effect of glycerol/lauric acid molar ratio on the esterification reaction, catalytic tests were performed with different glycerol/lauric acid molar ratios, i.e. 4:1, 6:1 and 8:1.

As can be seen in the Figures 3(a) and 3(b), the effect of glycerol/lauric acid molar ratio on the lauric acid conversion was insignificant beyond a ratio of 6:1. At lower ratio, significant improvement was achieved as more glycerol was available for effective contact with the relatively more viscous lauric acid. As a result, increases in the lauric acid and glycerol monolaurate yield were observed. Further increase to 8:1 meant significant dilution to the limiting reactant to bring about adverse effect to the reaction. However, it worth noting that the fatty acid conversion steadily increased with time with corresponding increase in glycerol monolaurate yield. In this respect, TBMMT catalyst offered an advantage over HO₃S-SBA-15 mesoporous catalyst (Hermida et al., 2011).

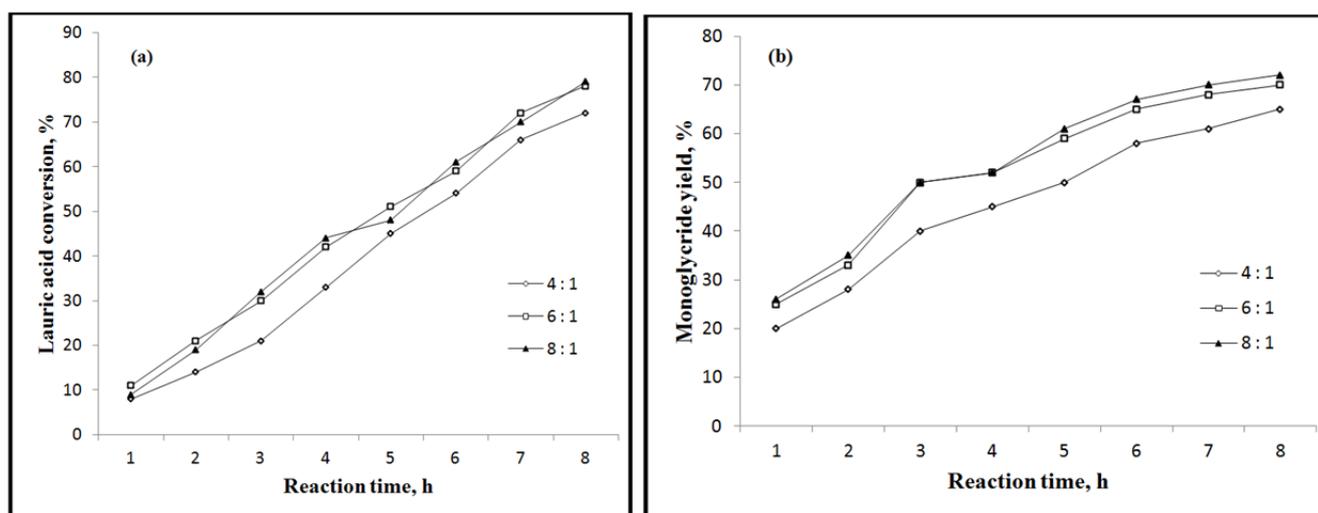


Figure 3. Effect of glycerol/lauric acid molar ratio on a) lauric acid conversion and b) monoglyceride yield in the glycerol esterification reaction. (Catalyst loading 3 wt. %, 130 °C).

Selectively to monoglyceride has been reported to be significantly influenced by the increase in glycerol/lauric acid molar ratio. Bossaert et al. (1999) observed the effect of glycerol/fatty acid ratio in their study between 1:1 to 6:1. They reported that the increase in glycerol/fatty acid ratios would increase the monoglyceride selectivity. The effect of glycerol/fatty acid ratios was somehow similar to that reported by Sanchez et al. (1997) using glycerol/fatty acid ratios from 1:3 to 3:1. This was because there was a larger chance for a fatty acid to react with glycerol to consequently result in an increase in

monoglyceride selectivity. As the fatty acid conversion also increased, corresponding increase in the monoglyceride yield was observed.

Conclusions

Geometrical constraint in the pores retarded the formation of higher glycerides. Fast reaction occurred within the first 8 h decreasing reactant concentration resulted in low rate of reaction after that. No further benefit was achieved above 3 wt. % of TBMMT catalyst loading due to liquid phenomena between the reactants and a reaction temperature of 130 °C and 6:1 for the reactant ratio were the optimum levels. Increasing catalyst loading improved glycerol monolaurate yield. Monoglyceride yield of about 70 % at corresponding lauric acid conversion of 80 % were achieved in 8 h at 130 °C using a glycerol/lauric acid molar ratio 6:1 and 3 wt.% of catalyst.. The modified montmorillonite catalyst show high catalytic activity and good selectivity to monolaurate. The behaviors were successfully correlated with the surface characteristic of the catalyst. Thus, TBMMT catalyst was an active catalyst to selectively produce glycerol monolaurate in the esterification reaction.

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