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# Synthesis of Glycerol Monostearate Over $K_2CO_3/\gamma\text{-}Al_2O_3$ Catalyst

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The synthesis of glycerol monostearate by transesterification of methyl stearate with glycerol can be carried out in the presence of basic catalyst. The absence of solvent in the reaction system would result in a low conversion of methyl stearate as a consequence of low miscibility between reactants. The addition N,N'-dimethyl formamide as solvent improved the activity of the catalyst and selectivity to glycerol monostearate. Different $K_2CO_3$-containing $\gamma\text{-}Al_2O_3$ catalysts were made and used in the reaction. The results showed that catalyst with higher basicity could lead to better reactant's conversion but poorer selectivity to glycerol monostearate and the optimal load of $K_2CO_3$ inducing the highest yield to glycerol monostearate was 20 % mass fraction of $\gamma\text{-}Al_2O_3$ supporter. At a glycerol/methyl stearate ratio of 6:1, 165 °C, 2 wt. % catalyst amount, a yield of 82.21 % of glycerol monostearate was achieved after 5h.

**Keywords: Glycerol monostearate, Methyl stearate, Glycerol, $K_2CO_3/\gamma\text{-}Al_2O_3$ catalyst, Solvent.**

## INTRODUCTION

Glycerol monostearate is amphiphilic molecule consist of a oleophilic fatty acid chain (C18) bonded to a hydrophilic glycerol molecule through an ester linkage. Such molecule structure reducing the interfacial tension between oil-water two phase enables to transform the two incompatible phase into a homogeneous disperse system with glycerol monostearate as mediator. Glycerol monostearate with a HLB (hydrophile-lipophile balance) value of 3.8 to 4.0 made it a typical non-ionic surfactant extensively applied in food, cosmetics, pharmaceutics, textile and fiber industries due to its excellent emulsifying, stabilizing, conditioning and plasticizing properties[1-6].

There are several main synthetic routes for obtaining glycerol monostearate *e.g.*, hydrolysis of triglyceride, esterification of glycerol with fatty acids or transesterification of glycerol with methyl stearate. Transesterification is a base catalyzed reaction and the industrial process generally use homogeneous basic catalyst leading to a mixture of mono-, di- and triglycerides (40 wt. : 50 wt. : 10 wt. %), device corrosion and environmental pollution[7]. Pure glycerol monostearate is generally obtained by molecular distillation process which further raises the production cost[8]. The use of solid basic catalyst, enzyme or ion exchange resin is a promising approach to replace alkaline catalysts[9-11]. It not only helps in minimizing difficulty in product separation, corrosion and environmental problem, but also increasing conversion to reactant and yield to glycerol monostearate.

Our objective is the transesterification of glycerol with basic solid catalysts in order to reduce by-product formation and allow an easier removal and recycle of catalyst. In the present work, we have prepared $K_2CO_3$-supported $\gamma\text{-}Al_2O_3$ catalyst with different loading amount which were never used in such reaction system. Then, the $K_2CO_3/\gamma\text{-}Al_2O_3$ solid basic catalysts were applied to catalyze the reaction. In addition, the influence of solvent such as DMF, ratio of glycerol/methyl stearate, temperature, catalyst dosage were investigated to throw light on their effect on yields of glycerol monostearate, which work out the optimal process route to achieve a higher yield of glycerol monostearate from the perspective of industrialization.

## EXPERIMENTAL

**Preparation of $K_2CO_3/\gamma\text{-}Al_2O_3$ catalyst:** Three different loading amount of $K_2CO_3/\gamma\text{-}Al_2O_3$ catalysts (labeled as KA-n, n refers to the capacity of $K_2CO_3$ as active material supported on $\gamma\text{-}Al_2O_3$ carrier; n = 10, 20, 30) were prepared by the isometric steep method. Corresponding amounts of $K_2CO_3$ (purity > 99 %) dissolved in aqueous solution were impregnated onto the particle form (40-80 mesh) of $\gamma\text{-}Al_2O_3$ supporter for 24 h in room temperature to acquire desired loading amount. The samples were dried at 100 °C for 10 h and calcined at 500 °C for 6 h and then sieved to desired fraction (40-80 mesh).

**Catalytic transesterification reaction of glycerol and methyl stearate:** The transesterification reactions were performed in a glass batch reactor equipped with a condenser system

(**Scheme-I**). A mixture of methyl stearate (7.46 g, 0.025 mol), glycerol with certain amount and $K_2CO_3$/γ-$Al_2O_3$ catalysts (different loading amount) was stirred and heated in a methyl silicone oil bath to the required temperature with or without DMF as solvent, under nitrogen atmosphere. A Dean-Stark instrument was adapted to the glass batch reactor to remove the methanol and recycle reflux DMF formed during the reaction. Samples were periodically taken out of the reactor and separated from the catalyst by centrifugation using chloroform as a solvent. Glycerol was separated from chloroform solution. Then, 1 μL of the sample was taken for gas chromatography analysis.

**Characterization of $K_2CO_3$/γ-$Al_2O_3$ catalyst and glycerol monostearate product[12]:** The base strength and alkali number of the catalyst were measured by indicator-benzoic acid titration method. The product mixture was analyzed by the gas chromatograph (Ouhua GC 9160) equipped with a DB-5Ht capillary column (15 m × 0.25 mm × 0.25 mm) by a flame ionization detector (FID). Nitrogen was used as a carrier gas with a flow rate of 2 mL/min. The injector and detector temperatures were 250 and 360 °C. To achieve good product separation, the column temperature was held at 50 °C for 0 min, increased to 180 °C at a rate of 15 °C/min and then raise to 230 °C at a rate of 7 °C/min, then continued to 380 °C at a rate of 20 °C/min and maintained for 6 min.

Conversion of methyl stearate ($X_{MS}$, with reference to the total ester content in the reactant), selectivity (S) and yield (Y) were calculated using following equations ($n_i$, mol of product i , GMS = glycerol monostearate, GDS = glycerol distearate, GTS = glycerol tristearate):

$$X_{MS}(\%) = \frac{n_{GMS} + 2n_{GDS} + 3n_{GTS}}{n_{GMS} + 2n_{GDS} + 3n_{GTS} + n_{MS}} \times 100$$

$$S_{GMS}(\%) = \frac{n_{GMS}}{n_{GMS} + 2n_{GDS} + 3n_{GTS}} \times 100$$

$$Y_{GMS}(\%) = X_{MS} \times S_{GMS} \times 100$$

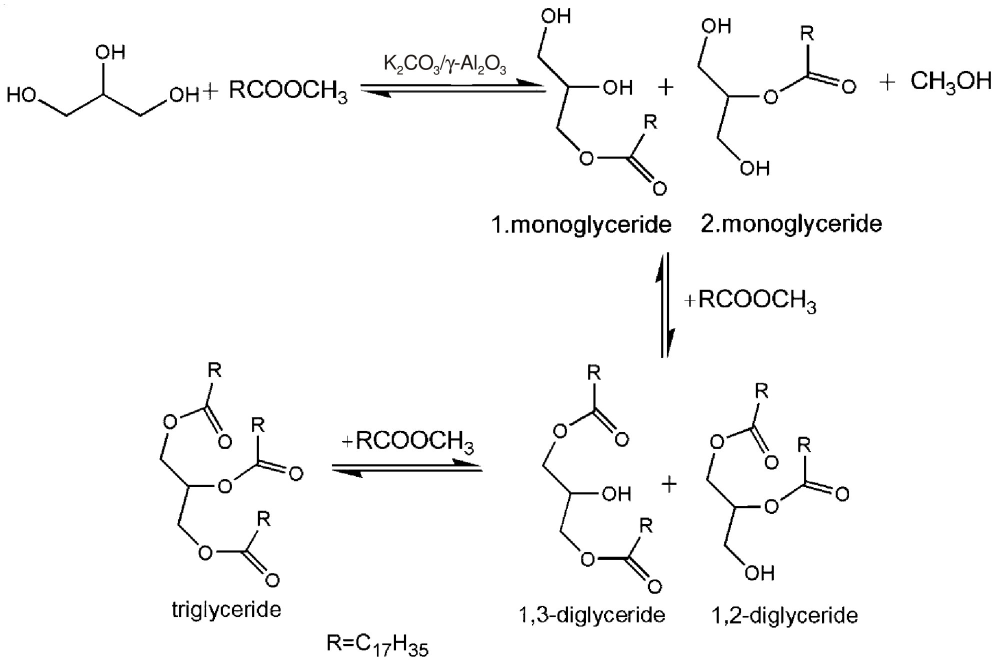
## RESULTS AND DISCUSSION

Result of basicity analysis of $K_2CO_3$/γ-$Al_2O_3$ catalyst were shown in Table-1. The weak base centers (9.3 < H- < 15) were found in KA-10, KA-20 and KA-30. The strong base centers (15 < H- < 22.3) resulting from the generating of K-O-Al substance containing electron-donating $O^{2-}$ anion were seen in KA-20 and KA-30 with the increase of $K_2CO_3$ loading. The K-O-Al substance was produced by the reaction of $K^+$ and hydroxyl group sticking to the surface of supporter in high temperature. The total alkali content (H- > 9.3) and weak base centers (9.3 < H- < 15) shown in KA-30 decreased and strong base centers (15 < H- < 22.3) increased comparing to KA-20. The excess $K_2CO_3$ loading amount leading to aggregation of $K_2CO_3$ on carrier surface would cover the γ-$Al_2O_3$ crystal crack and impede the interaction between actives and supporter.

TABLE-1
BASICITY STRENGTH, BASIC
SITES AMOUNT OF $K_2CO_3$/γ-$Al_2O_3$

| Catalyst | Alkali number/(mmol/g) | | |
|---|---|---|---|
| | H->9.3 | 9.3<H-<15.0 | 15.0<H-<22.3 |
| KA-10 | 0.42 | 0.42 | 0 |
| KA-20 | 1.68 | 1.33 | 0.35 |
| KA-30 | 1.47 | 1.02 | 0.45 |

The influence on reactant conversion and selectivity to glycerol monostearate by catalyst type were presented in Table-2. Conversion increased and time taken to reach equilibrium in reaction became shorter with more addition of $K_2CO_3$ on γ-$Al_2O_3$ supporter. The donating electron ability of catalyst contributing to transesterification enhanced with the increasing alkali number. The selectivity to glycerol monostearate was consistent with the number of weak base centers but contrary to that of strong base centers which may be



**Scheme-I:** Process for preparation of glycerol monostearate

TABLE-2
TRANSESTERIFICATION OF METHYL STEARATE USING DIFFERENT BASIC CATALYSTS

| Catalysts | Methyl stearate conversion (%) | Yield of glycerol monostearate (%) | Selectivity to glycerol monostearate (%) |
|---|---|---|---|
| KA-10 | 62.68 (11 h) | 53.97 | 86.11 |
| KA-20 | 97.45 (5 h) | 82.21 | 84.36 |
| KA-30 | 97.97 (5 h) | 56.97 | 58.15 |

responsible for the lower selectivity of glycerol monostearate in performing subsequent transesterification of glycerol monostearate formed during the reaction.

**Process optimization for glycerol monostearate:** To identify the optimum reaction condition, we took the following factors into consideration: Mole ratio of raw materials, reaction time, catalyst amount and effect of solvent (DMF).

**Effect of solvent:** The effect of solvent(DMF) was displayed in Fig.1. The active glycerol molecule got insufficient access to methyl stearate due to their immiscibility,which suppressed the process of transesterification. The reaction was accelerated because of increasing contact area between the two reactants with DMF as solvent.

In solvent-free system, large amount of methyl stearate continued to react with the newly produced glycerol monostearate leading to low selectivity to the target product. The addition of solvent would result in rapid transformation of methyl stearate in the beginning of the reaction. Thus subsequent transesterification of glycerol monostearate was inhibited to some extent due to weak concentration of methyl stearate in the system and the selectivity to glycerol monostearate was promoted.

**Influence of catalyst amount:** From the curves showing the influence of catalyst amount in Fig. 2. The conversion of methyl stearate increased and the time to reach equilibrium in reaction was cut down with the increasing dosage of catalyst. However, the impact of catalyst with dosage above 2 wt. % on the methyl stearate conversion was muted. Dehydration reaction restraining the transesterification of methyl stearate and producing more by-products such as polyglycerol could occur between glycerol molecules with excessive amount of alkali catalytic centers in the reaction system. Selectivity of glycerol monostearate decreased with increasing amount of KA-20 catalyst. Owing to excessive strong base centers, subsequent transesterification of glycerol monostearate formed during the reaction proceed resulting in the generation of glycerol distearate and glycerol tristearate.

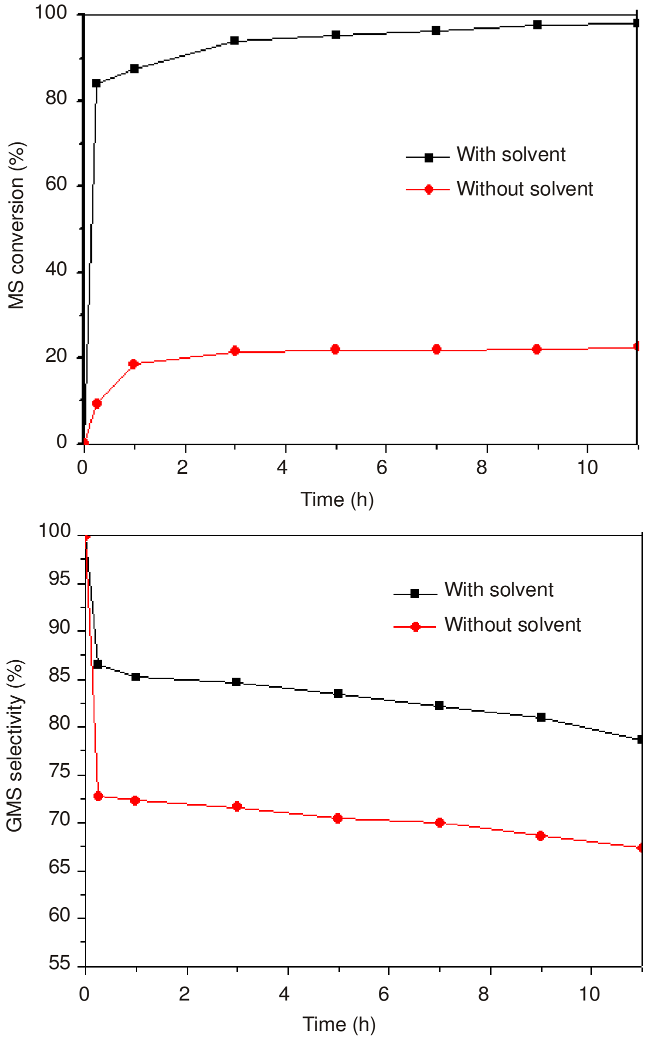


Fig. 1. Effect of solvent (DMF) on the methyl stearate conversion and selectivity to glycerol monostearate. (Reaction conditions: glycerol/methyl stearate molar ratio, 6:1; KA-20 amount, 2wt. %; reaction temperature, 165 °C)

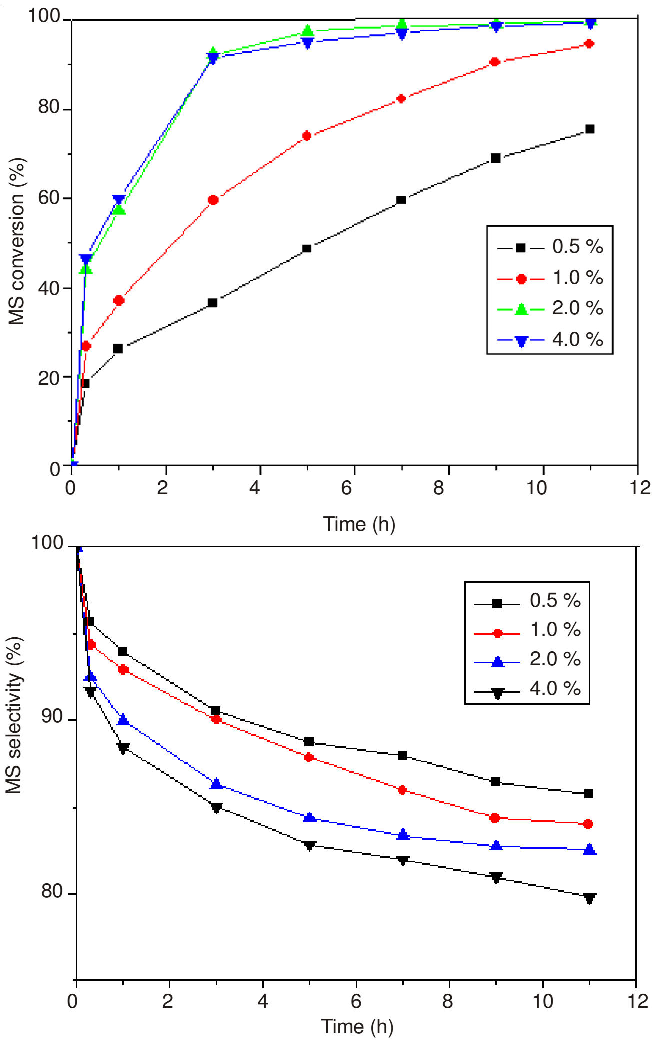


Fig. 2. Effect of catalyst amount on the methyl stearate conversion and selectivity to glycerol monostearate. (Reaction conditions: DMF as solvent; glycerol/methyl stearate molar ratio, 6:1; KA-20 catalyst; reaction temperature, 165 °C)

Taking the two factors above into consideration, the optimal dosage of KA-20 catalyst should be 2wt.%.

**Influence of mole ratio of glycerol and methyl stearate:** The influence of glycerol/methyl stearate molar ratio was shown in Fig. 3. The conversion of methyl stearate increasing with concentration of glycerol up could reach up to 100 % after 7 h with glycerol/methyl stearate molar ratio as high as 6 or more. More glycerin anions generated with excessive glycerin would reacted with methyl stearate rapidly, leading to the promotion of methyl stearate conversion therefore. Rapid depletion of methyl stearate could inhibit subsequent transesterification of glycerol monostearate formed during the reaction proceed resulting in the generation of glycerol distearate and glycerol tristearate. While excessive amounts of glycerol would lead to the increasing of material cost. To sum up, the mole ratio of glycerol/methyl stearate high as 6 was chosen.

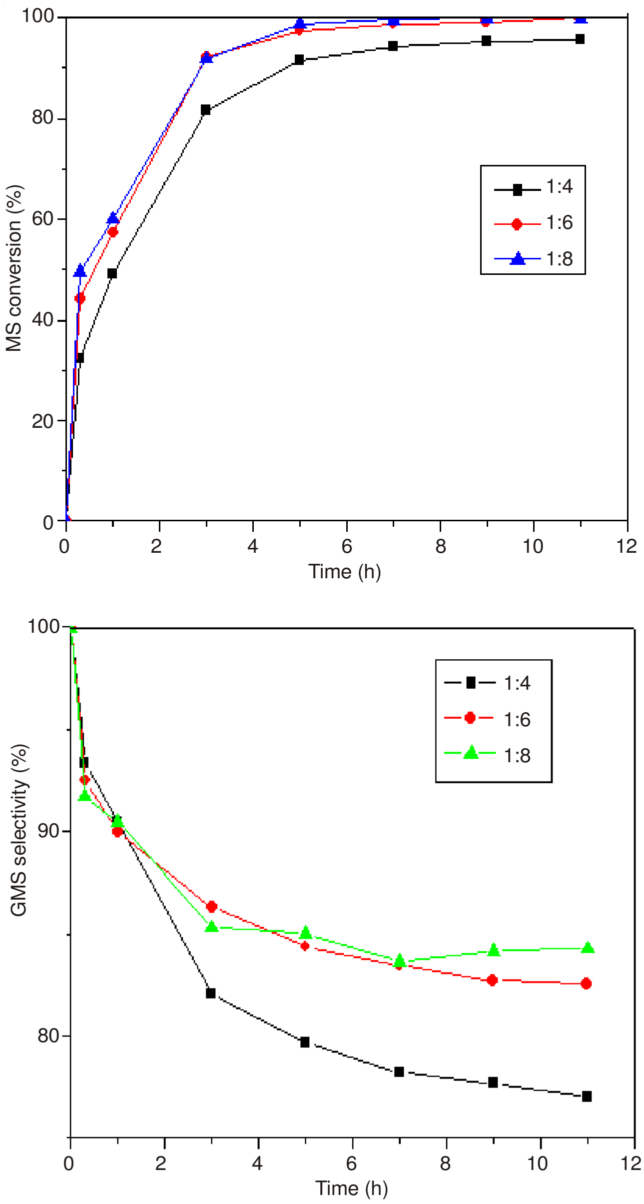


Fig. 3. Effect of glycerol/methyl stearate molar ratio on the methyl stearate conversion and selectivity to glycerol monostearate. (Reaction conditions: DMF as solvent; KA-20 catalyst, 2 wt. %; reaction temperature, 165 °C)

**Influence of temperature:** The curves showing the influence of temperature were seen in Fig. 4. Conversion of methyl stearate increased with rising temperature as an important factor in the endothermic reaction at the same reaction time. The methyl stearate conversion could reach up to 99 % after 7 h at 165 °C. Selectivity of glycerol monostearate was highest with reaction temperature as 105 °C, while the methyl stearate conversion was the lowest. In order to achieve the highest yield of glycerol monostearate, the reflux temperature of DMF (165 °C) was selected.

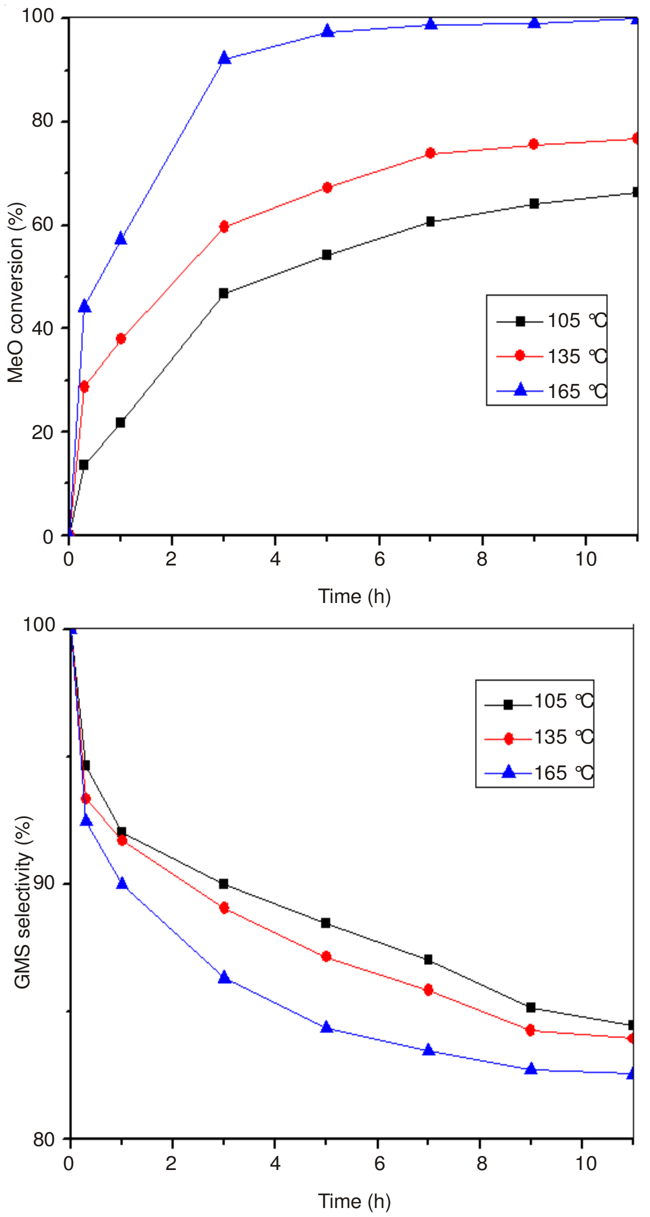


Fig. 4. Effect of temperature on the methyl stearate conversion and selectivity to glycerol monostearate (Reaction conditions: DMF as solvent; glycerol/methyl stearate molar ratio, 6:1; KA-20 catalyst, 2wt. %)

## Conclusion

Based on the results presented, DMF addition as solvent would improve the activity of catalyst and selectivity to glycerol monostearate obviously. $K_2CO_3$/γ-$Al_2O_3$ catalyst with more strong basic sites could lead to better reactant's conversion but poorer selectivity to glycerol monostearate. Selectivity of glycerol monostearate was consistent with the number of weak base centers but contrary to that of strong base centers which may be responsible for the lower selectivity of glycerol monostearate in performing subsequent transesterification of glycerol monostearate formed during the reaction. The optimal load of active material inducing the highest yield to glycerol monostearate was 20 % mass fraction of γ-$Al_2O_3$ supporter. At a glycerol/methyl stearate ratio of 6:1, 165 °C, 2 wt. % catalyst amount, a yield of 82.21 % of glycerol monostearate was achieved after 5 h.

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## REFERENCES

1. R. Pawongrat, X. Xu and A. H-Kittikun, *Food Chem*., **104**, 251 (2007).
2. F. Zeng, B. Yang, Y. Wang, W. Wang, Z. Ning and L. Li, *J. Am. Oil Chem. Soc*., **87**, 531 (2010).
3. R. Pawongrat, X. Xu and A. H-Kittikun, *J. Sci. Food Agric*., **88**, 256 (2008).
4. H. Ghamgui, N. Miled, A. Rebai, M. Karra-chaabouni and Y. Gargouri, *Enzyme Microb. Technol*., **39**, 717 (2006).
5. Z. Zhang and H.D. Goff, *Int. Dairy J*., **15**, 495 (2005).
6. M.L. Damstrup, T. Jensen, F.V. Sparso, S.Z. Kiil, A.D. Jensen and X. Xu, *J. Am. Oil Chem. Soc*., **82**, 559 (2005).
7. M. Gupta, Manufacturing Processes for Emulsifiers, In: Y.H. Hui (ed.), Bailey's Industrial Oil & Fat Products, 4, John Wiley & Sons, Inc., New York, pp. 569-601 (1996).
8. L.V. Fregolente, P.B.L. Fregolente, A.M. Chicuta, C.B. Batistella, R. Maciel Filho and M.R. Wolf-Maciel, *Chem. Eng. Res. Des*., **85**, 1524 (2007).
9. M. Trejda, K. Stawicka and M. Ziolek, *J. Appl. Catal. B*, **103**, 404 (2011).
10. C.A. Ferretti, S. Fuente, R. Ferullo, N. Castellani, C.R. Apesteguía and J.I. Di Cosimo, *J. Appl. Catal. A*, **413**, 322 (2012).
11. C.A. Ferretti, A. Soldano, C.R. Apesteguía and J.I. Di Cosimo, *Chem. Eng. J*., **161**, 346 (2010).
12. A.N. Dias, M.B.R. Cerqueira, R.R. Moura, M.H.S. Kurz, R.M. Clementin, M.G.M. D'Oca and E.G. Primel, *Fuel*, **94**, 178 (2012).