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REGULAR ARTICLE

Greener route for intensified synthesis of Tricaprylin using Amberlyst-15

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Abstract. Tricaprylin is a triglyceride of caprylic acid. Tricaprylin is a medium-chain triglyceride. Medium-chain triglycerides are considered as a nutraceutical and have a wide range of application in health foods and nutraceutical industry. In the present study, the synthesis of tricaprylin is investigated using environment-friendly approach i.e., with the application of microwave and heterogeneous catalyst dry acidic Amberlyst-15. The result of various reaction conditions like the molar ratio of reactant, reaction temperature, and catalyst amberlyst loading on the conversion of caprylic acid into tricaprylin is studied. The microwave synthesis is compared with traditional or normal synthesis of tricaprylin. In the present study, it is found that microwave synthesis resulted in a high degree of conversion in less time as compared to conventional synthesis. Conversion of 99.5% is observed in 16 min of reaction between medium-chain fatty acid (C8) and glycerol under optimized reaction parameters of the molar ratio of caprylic acid:glycerol as 3:5 with reaction temperature 800 °C and catalyst loading of 4% (by weight of fatty acid).

Keywords. Medium-chain triglyceride; caprylic acid; tricaprylin; microwave; esterification; neutraceutical.

1. Introduction

Triglycerides containing fatty acid from C6 to C12 are neutraceutical fat with various health benefits. Triglycerides with medium-chain fatty acid are considered as a source of energy which provides 8.4 kcal/g of energy.[1] Naturally, there is a limited source of medium-chain triglycerides which include coconut oil rich in lauric acid and palm kernel oil.[2] Medium-chain triglycerides have high satiety value as compared to oil like coconut oil, primarily containing lauric acid and other edible oil. Hence, it reduces food intake and is beneficial in weight loss.[3] Medium-chain triglycerides are conventionally synthesised by the reaction catalysed by enzyme between glycerol and fatty acid by the esterification reaction.[4] Lu *et al.,*[5] investigated synthesis of medium and long-chain triglycerides using enzyme in a medium free of solvent condition using interesterification reaction. The obtained yield was reported as 74.9% in 6 h. Selmi *et al.,*[6] reported the production of tricaprylin using enzyme immobilized lipase with a yield of 78% at 60 °C by the esterification reaction. The water eliminated during the reaction was determined using Karl-fisher measurement. Pan *et al.,*[7] studied the production of tricaprylin with use Ten 1,3-dialkylimidazolium base ionic liquids. A higher yield of 92.7% was reported at 66.7 °C. The ionic liquid was separated from the reaction mixture using centrifugation. Kwon *et al.,*[8] also studied the synthesis of medium-chain triglyceride using commercial lipases from different sources using an organic solvent. The activity of these lipases was different, some of them showed higher activity, whereas some showed low activity at given reaction condition. *C. rugosa* gave high production of dicaprin, *R. miehei* showed higher activity for production of tricaprin. Wong *et al.,*[9] gave the effect of the activity of enzyme lipase from *Candida rugosa* on enzymatic esterification reaction between fatty acid (Capric acid) and glycerol in the presence of an organic solvent. The author reported more production of di and tricaprin as compared to monocarpic with 100 mg *Candida rugosa*. Surat *et al.,*[10] reported in his review that microwave-assisted process has various advantages for organic synthesis including esterification reaction as this process is green and rapid process which gives a high yield of the product with reduced losses. Perin

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et al.,[11] studied microwave-assisted transesterification of castor oil catalysed by sulphuric acid immobilized in SiO_2. The reaction gave maximum yield by using a microwave-assisted process in 30 min as compared with the conventional process of 3 h. More *et al.,*[12] studied the effect of ultrasound pre-treatment on Chemical esterification reaction between glycerol and fatty acid (caprylic acid) using an acid catalyst. The author reported yield of 96.6% in 9 h. Deshmane *et al.,*[13] studied esterification of lauric acid using ultrasound process and reported high yield in less time of reaction. More *et al.,*[14] investigated esterification of caprylic acid with emerging technology like super-critical CO_2 pre-treatment using enzyme and reported 97.3% yield in 6 h of reaction. Mohod *et al.,*[15] used ultrasonic reactor of 4 l capacity for synthesis of triglycerides of medium-chain fatty acid by esterification reaction using an acid catalyst and reported 77.4% conversion of lauric acid in trilauric in 270 min.

Microwave irradiation is extensively used for organic synthesis. Microwave irradiation process is an environment-friendly process for chemical synthesis. Microwave irradiation results in instantaneous heating by coupling of microwave directly with the reaction mixture which results in an increase in temperature and increases the rate of reaction, leading to faster conversion.[10] All the esterification reaction used for the synthesis of MCT made use of an enzyme, but the rate of reaction was slow and enzymes are very specific to the substrate and are costly. Some reported synthesis of medium-chain triglycerides using an acid catalyst. Acid catalysts like sulphuric acid and hydrochloric acid are concentrated acids that need to be handled with care and they also result in the formation of dark colour product and require a higher temperature and are not reusable. Some studies used metal catalyst for the synthesis of medium-chain triglycerides but these catalysts also work at a higher temperature and are expensive and need an extra process of separation from the reaction mixture.[16] Ion exchange resin Amberlyst-15 is a dry acidic heterogeneous catalyst which is also used for esterification reaction which shows higher activity and is cost-effective and reusable.[17]

A critical study of the literature divulges that there is a need for a green, convenient and economical process for the synthesis of medium-chain triglyceride. In the present study, medium-chain triglyceride of caprylic acid is synthesized using Ion exchange resin Amberlyst-15 which is a strong acidic heterogeneous reusable catalyst with the application of microwave irradiation process which forms novelty of the process. The microwave-assisted process is compared with the conventional synthesis with respect to % conversion, time of reaction and temperature. This kind of research with the use of heterogeneous catalyst is not studied or reported in the literature.

2. Material and methods

2.1 *Material*

Caprylic acid was purchased from S.D. Fine chemical Pvt. Ltd., Mumbai. Glycerol was taken from S.D. Fine Chemical Pvt. Ltd. Mumbai. Amberlyst-15 a dry acidic catalyst was also obtained from S.D. Fine chemicals Pvt. Ltd. Mumbai. The reactant and catalyst were used as received.

2.2 *Experimental methodology*

2.2a Conventional method: Conventional synthesis of tricaprylin was carried out using esterification reaction using amberlyst -15 catalyst. The reaction set up is shown in Figure 1. The known quantity of reactant glycerol and Caprylic acid were weighed based on molar ratio and were taken in three-neck flask followed by the addition of a catalyst. All reactants were measured in grams. The reaction mixture was kept on a magnetic stirrer and the reaction mixture was heated at 180 °C, agitation of the reaction mixture was carried out using a magnetic needle throughout the reaction. The three-neck flask containing reaction mixture was connected to condenser for condensing water vapours which is a by-product of esterification reaction and these condensed vapours were collected in a separate collector. Before starting the reaction and addition of a catalyst, a sample was withdrawn from the reaction mixture to calculate the initial acid value and the reaction was monitored by estimating acid value after a fixed interval of five minutes and the rate of conversion was calculated based on reduction in acid value.

Figure 1. Experimental arrangement for conventional synthesis of tricaprylin.

2.2b Microwave irradiation process: An oven was used for microwave irradiation with power rated from 100-800 W. The known quantity of caprylic acid and glycerol were added into the beaker based on a molar ratio. The initial acid value of the sample was calculated. The known quantity of Amberlyst-15 was added into the reaction mixture. The beaker was kept into the microwave irradiation chamber. Reaction as monitored with an estimation of acid value at regular intervals. The percentage conversion was calculated based on the reduction in acid value.

2.3 *Method of analysis*

2.3a Acid value: The acid value is determined by acid-base titration. It gives a clear idea of the amount of free fatty acid present. According to AOAC official method, Te 1a-64 a known amount of sample (1 mL) was taken in a conical base glass beaker. To sample 20 mL, neutralized ethyl alcohol was added followed with phenolphthalein indicator and then it was titrated against 0.01 N KOH. The acid value is calculated as:-

$$\text{Acid value} = \frac{56 \times \text{ Normality of KOH } \times \text{ Volume in ml of KOH used}}{\text{Weight of oil sample}}$$

2.3b FTIR analysis: Shimadzu Spectrometer- 8400S was used for FTIR analysis of the sample. Acetone was used to dilute the sample and placed on sample casing for Infra-Red analysis.

2.3c High-performance liquid chromatography analysis: Progress of the reaction was determined using Shimadzu HPLC. The HPLC system comprised of RID 6A refractive index detector. HiQSil C18 was column used for the analysis of triglyceride. The mobile phase was a mixture of acetic acid and acetonitrile (6:94 V/V). The flow rate was kept 1 mL/min. The flow rate was maintained constant. 2 µL of sample was injected.

3. Result and Discussion

3.1 *Effect of molar ratio*

Change in molar ratio affects the conversion rate of caprylic acid. It is studied at constant temperature and catalyst loading of 80 °C and 4%, respectively. The percentage conversion is studied with a change of molar ratio of Caprylic acid: Glycerol from 3:1 to 3:5. The effect can be easily observed from the Figure 2, as the concentration of glycerol increases the rate of reaction also increases to some extend (i.e., 3:5 molar ratio of caprylic acid:glycerol) after that there was no appreciable increase. As the concentration of glycerol is increased it helps in absorbing water formed during reaction and reaction accelerates in a forward direction. The equilibrium shifts towards tricaprylin and higher conversion is obtained. Mohod *et al.,*[15] also reported an increase in glycerol concentration increases the rate of conversion of fatty acid and speeds up the reaction.

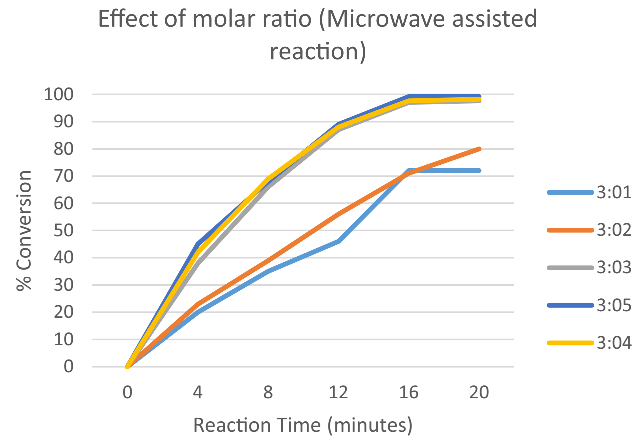

Figure 2. Effect of molar ratio of caprylic acid:glycerol on % conversion in microwave assisted reaction.

3.2 *Effect of amberlyst loading*

The influence of amberlyst loading on the rate of conversion is studied keeping molar ratio and temperature as 3:5 (Caprylic acid:Glycerol) and 80 °C, respectively. The effect of amberlyst-15 loading is clearly illustrated in Figure 3. The loading of Amberlyst was increasing from 1% to 5% (by weight of caprylic acid). It is observed that as the amberlyst concentration increases the rate of conversion also increases up to 4% catalyst loading, thereafter there is no observable change. Increase in catalyst loading

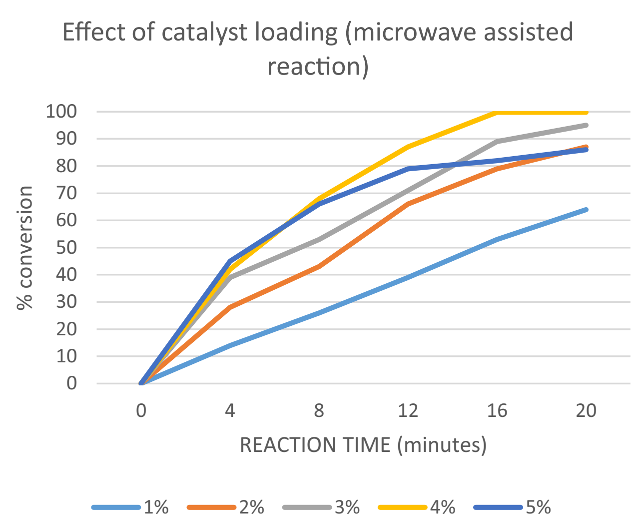

Figure 3. Effect of catalyst loading on % conversion in microwave-assisted reaction.

beyond 4% had a negative impact on the rate of conversion. As we are increasing catalyst concentration there is an increase in active sites which are available for the reaction and rate of conversion increase and the reaction drives in a forward direction. It is investigated that optimum catalyst loading for the maximum conversion was 4% Amberlyst.

3.3 *Effect of temperature of the reaction*

The influence of temperature of the reaction is studied on the rate of conversion keeping molar ratio and catalyst loading as 1:3 and 4%, respectively. The effect of temperature of reaction on the rate of conversion can be observed from Figure 4. The temperature of the reaction was studied from 50 °C to 100 °C. The increase in temperature increases the rate of conversion of caprylic acid to tricaprylin. The maximum conversion was observed at a temperature of 80 °C. As the temperature increases, the water is absorbed by the excess glycerol and removed rapidly from the reaction mixture which drives the reaction in a forward direction. Kim *et al.*,[4] also reported temperature effect on the rate of conversion of medium-chain triglyceride using an enzyme.

3.4 *Comparison between conventional and microwave synthesis*

Microwave irradiation synthesis of tricaprylin gave 99.5% conversion in 16 min with use of 4% heterogeneous catalyst Amberlyst-15 at 80 °C with a molar concentration of Caprylic acid: Glycerol as 1:3. The microwave process is compared with the conventional esterification synthesis of tricaprylin. The conventional synthesis gave only 10% conversion in 16 min at 80 °C. The conventional synthesis gave 94% conversion in 28 h of reaction time at optimized reaction conditions. This may be due to fact that in a conventional process that heat is first transferred to reaction vessel from there it is transferred to the reaction mixture which activates the reactant and then the process starts, hence there is improper heat transfer. On the other hand, in the microwave irradiation process, microwaves couple themselves with the molecules and there is rapid heating of reaction mixture, independent of the heat conductivity of reaction vessel. Hence, there is proper heat transfer which results in proper mass transfer and rate of reaction is driven in a forward direction.[10] The comparison is shown in Figure 5. It is clear from the present study that the microwave process is an eco-friendly and highly efficient process for the synthesis of tricaprylin.

3.5 *Acid value*

The conversion of the reaction was monitored by withdrawing a sample from the reaction mixture and estimating acid value at regular interval for both conventional and microwave irradiation process. The decrease in acid value indicates the conversion of fatty acid into tricaprylin. The rapid decrease in acid value in the microwave process confirmed an increase in the rate of reaction. The change in acid value is shown in Figure 6. Whereas in the conventional process, the change in acid value was slow indicating a slow rate of conversion. More *et al.*,[12] studied that the conversion of reactant to the product was observed by a reduction in the acid value of reaction mixture. From Figure 6 it can be seen that for microwave irradiation the initial

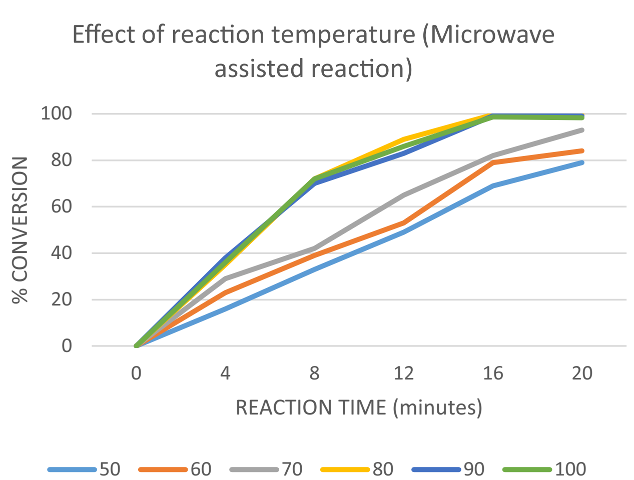

Figure 4. Effect of reaction temperature on % conversion in microwave-assisted process.

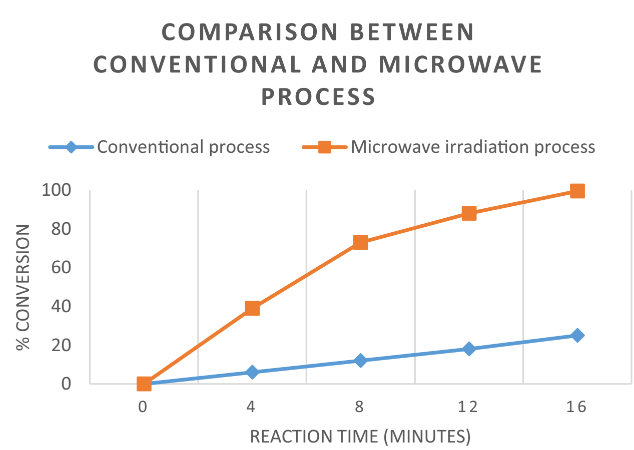

Figure 5. Comparison between conventional and microwave process.

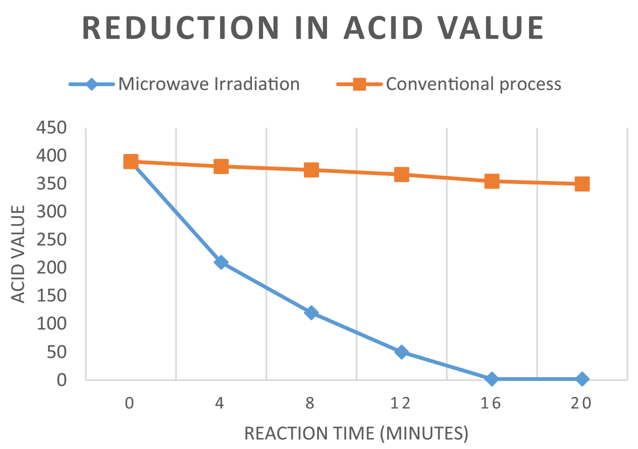

Figure 6. Reduction in acid value in microwave and conventional process.

acid value of 390 mg KOH has decreased to 1.7 mg KOH in 16 min of reaction, whereas it reduced to 350 mg KOH for conventional process in 16 min.

3.6 *Reusability of Amberlyst-15*

The reusability of Amberlyst-15 was confirmed by using the same catalyst for 8 cycles. The obtained result is represented in Figure 7. The catalyst was used for chemical esterification reaction of Caprylic acid (C8) and glycerol. After the completion of the reaction, the amberlyst-15 was removed from reaction mixture simply by filtration. It was washed, dried and was used again for another cycle esterification reaction. From Figure 7 it is found that Amberlyst can be reused for 5 cycles without a change in its catalytic activity. Beyond the Fifth cycle, the catalyst showed reduced activity and reaction time was found to increase with a reduced rate of conversion. The other reaction parameter like molar ratio, catalytic loading temperature and ultrasonic parameters were kept

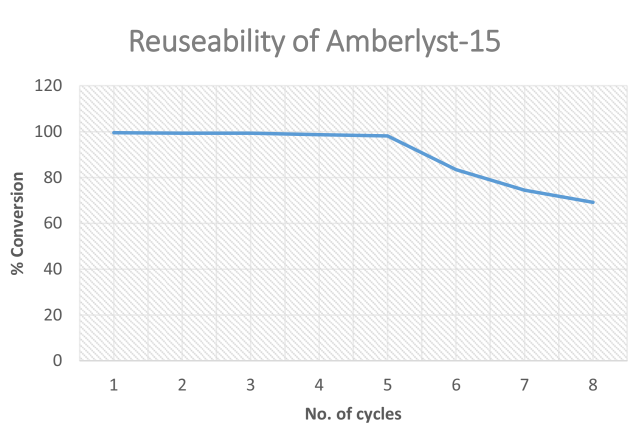

Figure 7. Reusability of Amberlyst-15 for 8 cycles of esterification reaction between caprylic acid and glycerol.

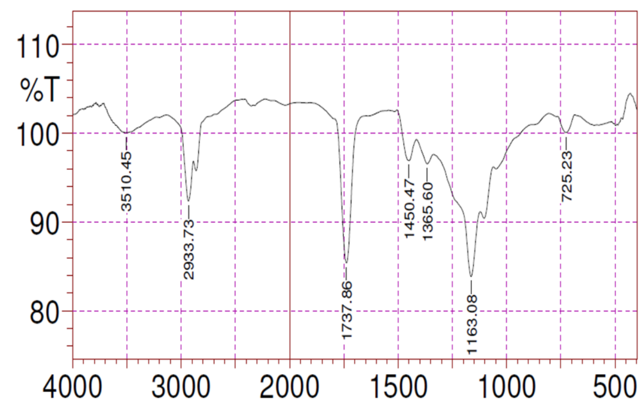

Figure 8. IR spectra of tricaprylin.

constant for all cycles. Zare *et al.*,[18] also reported reusability of Amberlyst-15 for 6 cycles for the synthesis of isoamyl acetate.

3.7 *FTIR*

The tricaprylin were characterized using FTIR analysis and it was confirmed by the strong peak at 1737.86 cm^{-1} corresponding to carbonyl group. The IR Spectra is shown in Figure 8. The peak at 2933.73 cm^{-1} corresponds to the carbon-hydrogen bond. Other than carbonyl peak and carbon-hydrogen peak, there are more peaks at 1450.47 cm^{-1} corresponds to carbon-hydrogen bending, 1365.60 cm^{-1} corresponds to none, 1163.08 cm^{-1} corresponds to strong carbon-hydrogen stretching of ester and peak at 725.23 cm^{-1} attributed to carbon-hydrogen bending.

3.8 *HPLC*

HPLC analysis was done for the final sample of tricaprylin for confirmation of formation of tricaprylin in the reaction. The tricapylin peak was seen at 6.7 retention time. Thus it confirmed the formation of tricaprylin in the reaction. More *et al.*,[12] also reported tricaprylin at retention time 6.7 by characterization using HPLC. HPLC result is shown in Figure 9.

4. Conclusions

Microwave synthesis of tricaprylin using dry acidic Amberlyst-15 catalyst is a novel, energy-efficient green and environment-friendly process. Microwave irradiation assisted process gave 99.5% conversion in 16 min of reaction time at 80 °C, 3:5 molar ratio of fatty acid (caprylic acid) to alcohol (glycerol) and 4%

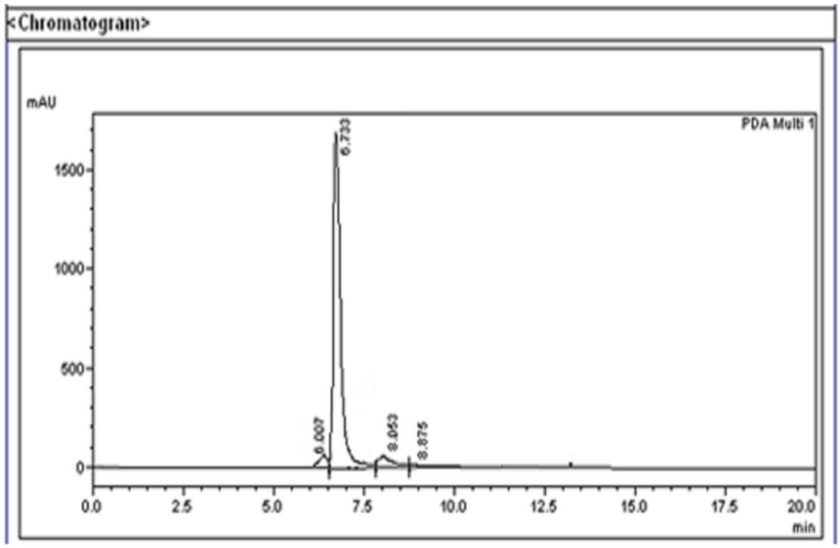

Figure 9. HPLC analysis of tricaprylin.

amberlyst loading. During microwave irradiation, there is a direct interaction of microwave with the reaction mass, which enhances the rate of heat and mass transfer and hence the reaction is pulled in a forward direction. Due to the use of excess glycerol, the water formed during the reaction was rapidly absorbed by glycerol shifting the equilibrium of reaction towards fatty acids. The microwave irradiation has been proved to be the best alternative to lengthy conventional synthesis of medium-chain triglycerides. The conventional process showed only 10% conversion in 16 min of reaction.

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Compliance with ethical standards

Conflict of interest The authors confirm that they have no conflicts of interest with respect to the work described in this manuscript.

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