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Short communication

Process intensification of synthesis process for medium chain glycerides using cavitation

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ABSTRACT

Cavitation results in conditions of local hot spots, turbulence and liquid circulation in the reactor which can result into intensification of chemical reactions. The present work investigates the effect of cavitating conditions on the synthesis process of medium chain glycerides (MCG) based on the esterification reaction between the fatty acids and glycerol. Effect of molar ratio and temperature on the rate of reaction and equilibrium conversion in the presence of ultrasound has been studied. It has been conclusively established that cavitation indeed results in substantial degree of intensification as compared to the conventional approach reported in the literature. Under optimized operating conditions of mole ratio (1:3) and temperature (90 °C), equilibrium conversion of 98.5% has been obtained in about 6 h of reaction time using cavitation.

1. Introduction

Glycerides of C8–C10 fatty acids, commonly known as medium chain glycerides (MCG), are useful in treating a number of medicinal disorders that involve impaired or damaged lipid metabolism, which include obstructive jaundice, billiary cirrhosis, pancreatitis, cystic fibrosis, celiac disease etc. In addition to the medical application and success of its use for malabsorption cases, many applications of medium chain glycerides, especially triglycerides, have been developed because of its unique physical and chemical characteristics and the absorption, transport and metabolism differences from the conventional fats and oils. The significant features of triglycerides which have recently evolved are that it appears to be a useful tool in the control of obesity, it appears to be a factor not only in the lowering of serum cholesterol but also in the inhibition and/or limitation of cholesterol deposition in the tissues, it appears to be a useful tool in providing higher levels of energy quickly, in both animal and humans. It is also reported to be useful for feeding newborn infants, both to assist their initial growth and contribute to their physiological development [1–3]. Medium chain glycerides, which are mainly a mixture of mono-, di- and triglycerides also have specific application in the field of foods, pharmaceuticals and cosmetics. Medium chain monoglycerides are ideal solvent for aromatics, steroids, dyes and perfume bases. A mixture of medium chain monoglycerides and diglyceride was found to be an effective solvent for dissolving cholesterol gallstones in humans [4].

Glycerides are generally synthesized by the process of esterification between fatty acids and glycerol [4–8]. Kim and Rhee [4] studied the enzymatic synthesis of MCGs by using capric acid and glycerol as substrates in the presence of immobilized lipase (*Rhizomucor miehei*) without any solvent or surfactant. The obtained extent of conversion was about 90% on the basis of capric acid consumption in about 10 h reaction time. Selmi et al. [5] investigated synthesis of triglycerides using immobilized lipase in solvent free medium and reported that the rate of reaction was much slower for the medium chain fatty acids as compared to the C14–C18 chain length. Dıaz et al. [6] studied the esterification of lauric acid (C12) with glycerol by using hybrid MCM-41 materials containing simultaneously alkyl and sulfonic acid group catalyst and reported that at a operating molar ratio of fatty acid to glycerol as 1:3 and a temperature of 100 °C, about 90% conversion is obtained in 24 h. In general the reaction times of more than 24 h have been reported to get more than 95% conversion based on the fatty acids [5–9]. Thus, it becomes imperative to look for ways for intensification of this synthesis process. Cavitation has been recently reported to be a useful tool for intensification of chemical reactions [10].

Cavitation can be in general defined as the generation, subsequent growth and collapse of the cavities releasing large magnitudes of energy over a very small location resulting in very high energy densities [11–13]. Cavitation occurs at millions of locations in the reactor simultaneously and generates conditions of very high temperatures and pressures (few thousand atmospheres pres-

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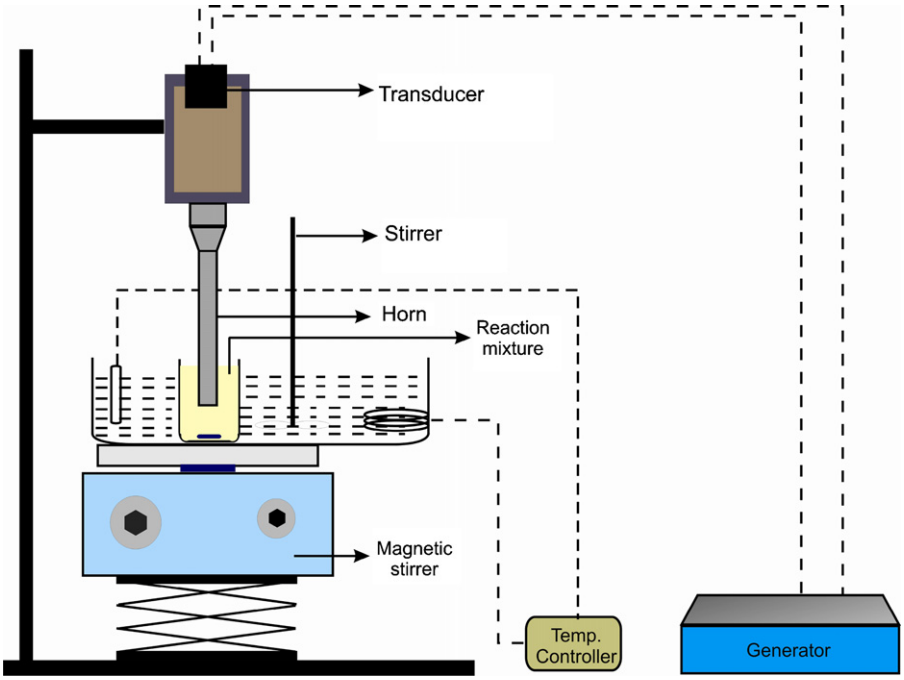

Fig. 1. Schematic representation of the experimental setup.

sure and few thousands K temperature) locally with overall ambient conditions [13]. Thus the chemical reactions requiring severe conditions can be effectively carried out using cavitation at ambient conditions. Moreover free radicals are generated in the process due to the dissociation of vapours trapped in the cavitating bubbles, which results in either intensification of the chemical reactions or may even result in the propagation of certain reactions [14,15]. Cavitation also results in the generation of local turbulence and liquid micro-circulation (acoustic streaming) in the reactor enhancing the rates of the transport processes [12,15]. These mechanical effects of cavitation are mainly responsible for the intensification of physical processing applications and also chemical processing applications limited by mass transfer, whereas the chemical effects such as generation of hot spots and reactive free radicals are responsible for the intensification of chemical processing applications. The present work investigates the effect of cavitating conditions on the synthesis process of medium chain triglycerides based on the esterification reaction between the fatty acids and glycerol. Comparison has also been made with some of the literature illustrations [6,17,18] reporting conventional approach based on use of stirring. The aim has been to qualitatively establish the efficacy of cavitational reactors in intensifying the synthesis of medium chain triglycerides. It has to be noted here that no such study has been reported in the literature to the best of our knowledge and hence the current work represents a significant advance in the synthesis process of medium chain triglycerides.

2. Materials and methods

2.1. Chemical reaction scheme

The reaction considered for the present study is an esterification reaction between C8–C10 fatty acids and glycerol with H_2SO_4 as a catalyst. The steps in the reaction are as follows:

$$\text{FA} + \text{glycerol} \overset{98\%\,H_2SO_4}{\rightleftarrows} \text{monoacyl glycerol} + H_2O$$

$$\text{FA} + \text{monoacyl glycerol} \overset{98\%\,H_2SO_4}{\rightleftarrows} \text{diacyl glycerol} + H_2O$$

$$\text{FA} + \text{diacyl glycerol} \overset{98\%\,H_2SO_4}{\rightleftarrows} \text{triacyl glycerol} + H_2O$$

Here, monoacyl glycerol (MAG) and diacyl glycerol (DAG) are the intermediates and triacyl glycerol (TAG) is the final product. All three reactions are reversible endothermic reactions requiring continuous energy supply and overcoming equilibrium limitations.

2.2. Materials

The fractions of C8–C10 fatty acids and glycerol were gift samples from Godrej Industries Ltd. (Mumbai, India). The fatty acid composition included 60.35% caprylic acid, 38.11% capric acid and 1.15% lauric acid. Sulphuric acid (98%) was procured from Merck (India) Ltd. Mumbai whereas Sodium hydroxide was procured from S.D Fine-Chem Pvt. Ltd., Mumbai, India.

2.3. Experimental setup

The experimental setup used for the current study has been depicted schematically in Fig. 1. Ultrasonic horn, device used for the generation of cavitation, was procured from M/s. Dakshin, India which operates at a frequency of 22.5 KHz, with the rated power of 240 W and calorimetric efficiency (ratio of actual energy used for generation of cavitation events to the supplied electrical energy) as 7%. The reactions were carried out in a beaker of 100 ml capacity where the reaction volume (~85 ml) was kept constant for all the reactions. It was equipped with a water bath with stirrer to maintain the reaction mixture at a constant temperature. The magnetic stirrer was also provided to stir the glycerol phase.

2.4. Experimental procedure

Initially, a known quantity of fatty acids was taken in the beaker and glycerol was added based on the selected molar ratio. To this mixture, 5% H_2SO_4 (by weight with respect to fatty acids) was added

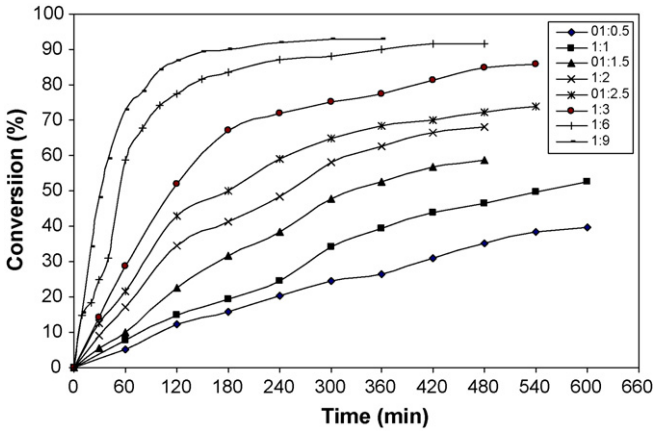

Fig. 2. Effect of molar ratio of fatty acid to glycerol on the extent of conversion.

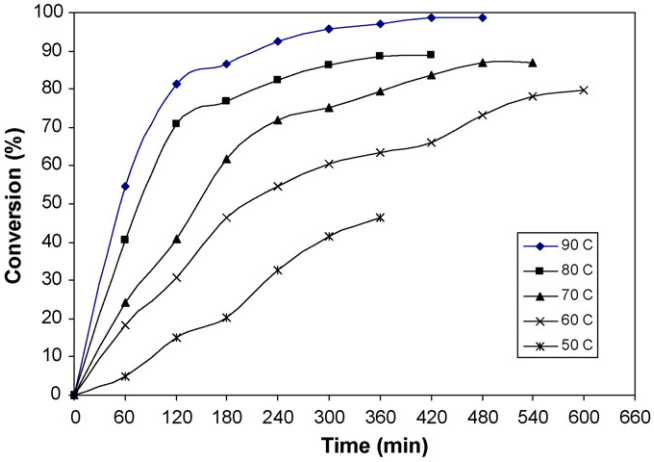

Fig. 3. Effect of reaction temperature on the extent of conversion.

with stirring. The resultant reaction system is heterogeneous with two immiscible liquid phases (glycerol and fatty acid). Magnetic stirrer was used to stir the glycerol phase (lower phase). Ultrasonic horn was then dipped into the reaction mixture with fixed distance (1 cm) away from the interface between glycerol phase and fatty acid phase. Sonication of reaction mixture was then started and samples from the fatty acid phase (upper phase) were taken out at periodic time intervals. The reaction mixture samples were titrated with 0.5 N NaOH solution to determine the amount of unconverted fatty acid in terms of acid value. During this study, effect of acid to glycerol molar ratio and operating temperature on the rate of the reaction and equilibrium conversion in the presence of ultrasound has been studied. The experiments were repeated to check the reproducibility of the obtained results and the experimental errors were observed to be in the range of ±2%.

3. Results and discussion

3.1. Effect of molar ratio

Effect of molar ratio on the rate of reaction was investigated at a constant reaction temperature (70 °C), catalyst concentration (catalyst used is 98% H_2SO_4 at a loading of 5 wt% of fatty acid) and constant height of tip of ultrasonic horn from the interface (1 cm) between fatty acid and glycerol. The reaction was studied over a wide range of molar ratio of FA to glycerol (1:0.5–1:9) and the obtained results have been given in Fig. 2. It can be easily seen from the figure that the reaction performance is significantly affected with the change in molar ratio of fatty acid to glycerol till an optimum ratio of 1:6 beyond which only marginal increase has been observed. This can be attributed to the fact that with a change in the molar ratio of FA to glycerol from 1:0.5 to 1:6, the available quantity of glycerol to take up water formed during the esterification reaction increases. Due to enhanced removal of one of the products of reaction, equilibrium shifts towards the right and higher extents of conversion with respect to fatty acid is obtained. Also the extent of cavitational intensity is expected to be higher at higher concentration of glycerol in the system as compared to the fatty acid due to the fact that physicochemical properties favor the formation of the nuclei. It also appears that the extent of water formed and that removed at 1:6 ratio of FA to glycerol is perhaps marginally different and hence any further increase in the ratio does not lead to significant changes in the equilibrium conversions. Kelkar et al. [16] have also reported similar results for intensification of esterification of acids for synthesis of biodiesel using acoustic and hydrodynamic cavitation.

It should also be noted here, that at an operating molar ratio of FA to Glycerol as 1:6 or 1:9 (maximum quantity of Glycerol), even though the extent of conversion obtained is higher, the unreacted glycerol significantly adds to the separation load, which can alter the overall economics of the synthesis process at industrial scales of operation. Thus these ratios have not been selected for further studies related to the effect of operating temperature and an operating ratio of 1:3 has been considered.

3.2. Effect of reaction temperature

The reaction temperature was varied from 50 °C to 90 °C with a constant molar ratio of fatty acid to glycerol (1:3), constant catalyst concentration (catalyst used is 98% H_2SO_4 at a loading of 5 wt% of fatty acid) and ultrasonic horn position with respect to the interface. The effect of temperature on this esterification reaction has been shown in Fig. 3. The reaction was studied to the stage where it practically reaches the equilibrium conversion (where there in no reduction in acid value on increasing the reaction period). It can be seen that the change in temperature affects not only the rate of reaction but also the equilibrium conversion. Maximum rate of reaction and equilibrium conversion has been obtained at an operating temperature of 90 °C. This is due to the fact that esterification reactions are endothermic in nature as well as it might be due to the increased ability of glycerol to take up water formed during the reaction with an increase in the operating temperatures, especially beyond 70 °C. Dıaz et al. [6] and Selmi et al. [5] have also reported similar effect of operating temperature on the extent of conversion for synthesis of medium chain triglycerides.

It should also be noted here that the effect of operating temperature in the presence of cavitating conditions needs to be further investigated at still higher operating temperatures. Due to the limitations of the present experimental setup in terms of bonding of the transducers to the ultrasonic reactors, the operating temperature was limited to 90 °C.

3.3. Comparison with conventional synthesis methods

Under optimized operating conditions of 90 °C reaction temperature, molar ratio of FA to Glycerol at 1:3 and 5% catalyst concentration, equilibrium conversion of about 98.5% has been reached in 6 h in the presence of ultrasound. Comparison has been done with some of the more traditionally used methods of synthesis for qualitatively ascertain the effect of cavitating conditions on the synthesis process. Dıaz et al. [6] reported that with similar

operating conditions (molar ratio of fatty acid to glycerol as 1:3 and a temperature of 100 °C) but with out the use of ultrasonic irradiation, about 90% conversion was obtained in 24 h. Halldorsson et al. [17] have also reported that 24 h of reaction time was required to get more than 90% yields of the structured triacylglycerols based on the combined chemical and enzymatic route. Medina et al. [18] also reported that about 95% yield of triglycerides is obtained in 72 h of reaction time at an operating temperature of 50 °C and under similar operating molar ratio of fatty acid to glycerol (1:3). Thus, it can be said that there is a significant intensification in the rates of esterification reaction for synthesis of medium chain glycerides in the presence of cavitating conditions. Also the synthesis is possible at much less severe conditions, in terms of operating temperature and requirement of vacuum, using cavitational reactors as compared to conventional approach as reported in the literature.

4. Conclusions

Cavitation can be effectively used for intensification of esterification process for synthesis of medium chain glycerides. By the use of cavitation induced by ultrasonic irradiations, the reaction time decreases from about 24 h observed in traditionally used chemo or enzymatic routes as reported in the literature to about 6 h due to enhanced rate of mass transfer, better mixing and local rise in the temperature by way of generation of cavitational hot spots. Maximum equilibrium conversion of 98.5% was observed at 90 °C and 1:3 molar ratio of fatty acid to glycerol in 6 h by the use of ultrasonic cavitation.

References

[1] V.K. Babayan, Medium-chain length fatty acid esters and their medical and nutritional applications, J. Am. Oil Chem. Soc. 58 (1981) 49A–51A.
[2] A.C. Batch, V.K. Babayan, Medium-chain triglycerides: an update, Am. J. Clin. Nutr. 36 (1982) 950–961.
[3] S. Nandi, S. Gangopadhyay, S. Ghosh, Production of medium chain glycerides from coconut and palm kernel fatty acid distillates by lipase-catalyzed reactions, Enzyme Microbial. Technol. 36 (2005) 725–728.
[4] S.M. Kim, J.S. Rhee, Production of medium-chain glycerides by immobilized lipase in a solvent-free system, J. Am. Oil Chem. Soc. 68 (1991) 499–501.
[5] B. Selmi, E. Gontier, F. Ergan, D. Thomas, Effects of fatty acid chain length and unsaturation number on triglyceride synthesis catalyzed by immobilized lipase in solvent-free medium, Enzyme Microbial. Technol. 23 (1998) 182–186.
[6] I. Dıaz, C. Márquez-Alvarez, F. Mohino, J. Perez-Pariente, E. Sastre, Combined alkyl and sulfonic acid functionalization of MCM-41-Type silica. Part 2. Esterification of glycerol with fatty acids, J. Catal. 193 (2000) 295–302.
[7] M. Linder, N. Kochanowski, J. Fanni, M. Parmentier, Response surface optimization of lipase-catalysed esterification of glycerol and $n-3$ polyunsaturated fatty acids from salmon oil, Process Biochem. 40 (2005) 273–279.
[8] Y. He, F. Shahidi, Enzymatic esterification of $n-3$ fatty acid concentration from seal blubber oil with glycerol, J. Am. Oil Chem. Soc. 74 (1997) 1133–1136.
[9] Z.Y. Li, O.P. Ward, Lipase-catalyzed esterification of glycerol and $n-3$ polyunsaturated fatty acid concentrate in organic solvent, J. Am. Oil Chem. Soc. 70 (1993) 745–748.
[10] L.H. Thompson, L.K. Doraiswamy, Sonochemistry: science and engineering, Ind. Eng. Chem. Res. 38 (1999) 1215.
[11] P.R. Gogate, Cavitational reactors for Process Intensification of chemical processing applications: A critical review, Chem. Eng. Proc. 47 (2008) 515–527.
[12] F.R. Young, Cavitation, McGraw Hill, London, UK, 1989.
[13] T.G. Leighton, The Acoustic Bubble, Academic Press, London, UK, 1994.
[14] J.L. Luche, Synthetic Organic Chemistry, Plenum Press, New York, USA, 1999.
[15] J. Lindley, T.J. Mason, Use of ultrasound in chemical synthesis, Chem. Soc. Rev. 16 (1987) 275.
[16] M.A. Kelkar, P.R. Gogate, A.B. Pandit, Intensification of esterification of acids for synthesis of biodiesel using acoustic and hydrodynamic cavitation, Ultrason. Sonochem. 15 (2008) 188–194.
[17] A. Halldorsson, C.D. Magnusson, G.G. Haraldsson, Chemoenzymatic synthesis of structured triacylglycerols, Tetrahedron Lett. 42 (2001) 7675–7677.
[18] A.R. Medina, L.E. Cerdán, A.G. Giménez, B.C. Páez, M.J.I. González, E.M. Grima, Lipase-catalyzed esterification of glycerol and polyunsaturated fatty acids from fish and microalgae oils, J. Biotechnol. 70 (1999) 379–391.