Energy Conversion and Management 138 (2017) 577–586

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Intensification of monostearin (phase change material) synthesis in infrared radiated rotating reactor: Optimization and heterogeneous kinetics

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A R T I C L E   I N F O

Article history:
Received 2 January 2017
Received in revised form 9 February 2017
Accepted 10 February 2017

Keywords:
Monostearin synthesis
Phase change material
Heterogeneous reaction kinetics
Far infrared radiation
Rotating batch reactor
Energy-efficiency

A B S T R A C T

The present article offers an intensification effort for the synthesis of glycerol monostearate (monostearin, a phase change material) using Amberlyst 36 (wet) catalyst. This work demonstrates the superiority of rotating batch reactor (RBR) over the stirred batch reactor (SBR) in glycerol (GL) – stearic acid (SA) esterification under far infrared radiation (FIRR). RBR depicted 92 ± 1% monostearin yield, which is 40% higher than the yield obtained in SBR under optimal process condition viz., 20:1 GL: SA mole ratio, 363 K reaction temperature, and 6.0 wt.% catalyst concentration in only 25 mins. The speed regimes for mass transfer limitation and surface kinetics controlled were determined using Mears criterion. The heterogeneous surface reaction kinetics in RBR followed Langmuir Hinshelwood (LH) mechanism ($R^2 = 0.98$) under resultant optimal condition. The reaction activation energy for the two different reactor configurations indicated that under identical operating conditions, SBR consumed almost double the energy required for RBR; thus representing superior energy-efficiency of RBR. Notably, the optimally synthesized monostearin demonstrated desirable properties of phase change material as confirmed by FTIR, TGA and DSC analyses.

1. Introduction

The most serious threat to mankind in the 21st century is global warming owing to augmented greenhouse gas emissions [1]. The demand for the energy requirements to achieve a comfortable environment has continuously increased worldwide. Thus, energy consumptions for heating, cooling and air conditioning, have increased the level of greenhouse gas emissions while reducing fossil fuel resources [2]. Therefore, energy-saving through energy-storage has become utmost crucial in engineering applications. Thermal energy-storage plays an important role for an effective energy-utilization through not only reducing the mismatch between supply and demand but also improving the performance and reliability of energy-systems [3].

In past years, several researchers developed monoester of glycerol (GL) through catalytic esterification of GL with stearic acid (SA) which found widespread applications in cosmetic, pharmaceuticals [4] and most significantly as engine lubricants due to its surface-active nature [5]. More recently, researchers have paid attention to the production of SA esters for applications as thermal-storage or phase change material [6]. Notably, fatty acid esters possess solid–liquid phase-change characteristics within a narrow temperature range and portray non-corrosive nature in contrast to fatty acids [7].

Preceding literature revealed the applications of homogeneous catalysts viz. sulfuric acid, nitric acid and p-toluene sulfonic acid for catalyzing esterification reactions [8,9]. The catalytic activity of homogeneous catalysts is high. However, because of their corrosive nature and the occurrences of side reactions, these catalysts cannot be effortlessly separated from the reaction mixture [10]; thus, making their usage economically unfavorable. Hence, in recent years the uses of solid acid catalysts have received noteworthy attentions. Recent studies illuminate the huge applications of Amberlyst-type ion-exchange resin catalysts for heterogeneous esterification reactions [11]. Amberlyst 36(wet) is one of the highly active solid acid catalysts with good ion-exchange capabilities, acceptable endurance towards high temperature, ample surface acidity; thus, demonstrating high efficacy in fatty acid esterification [12]. Furthermore, most of the previous works relevant to glycerol monostearate (monostearin) synthesis depicted requirement of either long reaction time [13] or high reaction temperature [14] coupled with low ester yield [15]. Accordingly, there is an

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http://dx.doi.org/10.1016/j.enconman.2017.02.026

utmost necessity to reduce the reaction time as well as reaction temperature for improved energy-efficiency and reduced production cost.

The rotating reactor has been applied previously for fatty acid conversion purpose; wherein instead of using mechanical impeller, rotating action has been employed to overcome the mass transfer resistance in heterogeneously catalyzed reactions. In rotating reactor [16], the centrifugal force generated due to the rotating movement of the reactor itself facilitates overcoming the mass transfer resistance to the transport of reactants from the bulk phase to the catalyst surface. Recently, electromagnetic radiation viz., far infrared radiation (FIRR) has gained immense attention in expediting methanol-oleic acid esterification reaction [17]. It was evident from past research work that FIRR could promote intense molecular collision coupled with more uniform heating; thus, reducing the activation energy and time requirement for esterification reactions in comparison with other energy sources [18]. However, combined application of FIRR and rotating batch reactor (RBR) for greater energy-efficiency and improved product selectivity has not been reported previously.

Taguchi experimental design (TED) [19] has been accepted as a robust method for optimization of the process parameters with minimum experimentations; besides, it reveals the interactive-effects among the process parameters in governing the process response.

Therefore, in the present study, FIRR has been applied for intensification of catalytic esterification of GL with SA for the maximization of monostearin (MSN) yield for application as phase change material. A rotating reactor under FIRR has been employed to compare MSN yield with that obtainable using a reactor fitted with mechanical impeller under optimal conditions, which have been determined through TED of the variables (viz. mole ratio, time, catalyst concentration and rotating speed). Amberlyst 36 catalyzed heterogeneous esterification kinetics has been evaluated under both mass transfer and surface reaction controlled regimes. Esterification activation energies under both the reactor configurations have been calculated for evaluating the advantage of rotating action over conventional stirring under FIRR.

2. Materials and methods

2.1. Materials

AR grade chemicals viz. GL (99.5%), SA (Loba India 99%), KOH (pellets), oxalic acid, toluene and isopropanol (MERCK) were purchased. Amberlyst-36 (wet) catalyst was procured from Sigma Aldrich while molecular sieves were supplied by SRL (India). The physical and chemical properties of the catalyst are tabulated in Table S1 of the supplementary document.

2.2. Experimental procedure and design of experiment

GL-SA esterification was carried out in both far infrared radiated rotating batch reactor (FIRR-RBR) and far infrared radiated stirred batch reactor (FIRR-SBR). The SBR was equipped with a turbine type mechanical stirrer (material of construction: 318 stainless steel) comprising of 6 blades (each length: 14 mm and width: 2 mm) attached to a central shaft (length: 310 mm and diameter: 7 mm). Primarily, the reaction was performed in FIRR-RBR (150 W) that consisted of a one-necked flask with a condenser holding the specific amount of molecular sieves (30 wt.% of SA) for removal of water produced during the reaction. At first, GL was added to the FIRR-RBR; as the temperature attained the preset value (353–373 K), pre-heated SA along with Amberlyst-36 catalyst was added to the FIRR-RBR operated over the rotational speed range of 50–300 rpm. The GL to SA molar ratios were maintained at 20:1, 15:1 and 10:1. The efficacy of RBR was compared with SBR over a speed range from 50 to 300 rpm. Additionally, in order to evaluate the advantage of using FIRR system, the optimal esterification run was also conducted in RBR equipped with a conventional heating (CH) system (CH-RBR) of same power input (150 W).

The independent factors and their corresponding levels were examined in an L_9 orthogonal array using standard TED [20]. Accordingly, the experiments were conducted in triplicates using three levels of the selected four operating factors viz., GL to SA mole ratio ($\theta_{GL:SA}$), reaction temperature (θ_{RT}), reactor rotational speed (θ_{RPM}) and catalyst concentration (θ_C) in GL-SA esterification. A customized set of nine experimental runs were presented in Table 1 with corresponding yields and SN ratios. After each experimental run of specified duration (25 min), the reaction mix was collected and the upper layer containing ester and unreacted SA (with traces of glycerol) was separated from GL-catalyst containing lower-layer by centrifugation. Subsequently, the upper-layer was cooled for separation of ester through crystallization (solidification). The ester so collected was used for GC–MS analyses for quantification of product components.

Acid number (A_{SA}) of ester layer and corresponding SA conversion (γ_{SA}) were calculated through direct titration method using Eqs. (1) and (2):

$$A_{SA} = \frac{56.11 \times M_{KOH} \times V_{KOH}}{m_{MSN}} \tag{1}$$

$$\gamma_{SA} = \left[\frac{A_{SA,final} - A_{SA,initial}}{A_{SA,initial}} \times 100\right] \tag{2}$$

TED computed the optimal factorial combinations pertaining to maximum MSN yield (ϕ_{MSN}) (Eq. (3)) through SN ratios (Eq. (4)) and analysis of variance (ANOVA) using MINITAB-17 (Minitab Inc. USA for Windows7) software.

$$\phi_{MSN} = \frac{\text{moles of (Monostearin) formed}}{\text{moles of Stearic acid consumed}} \times 100 \tag{3}$$

$$SN = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{\phi^2_{MSN,i}}\right) \tag{4}$$

Here, i denoted number of replications and n implied number of trial experiments executed in a particular factorial set values as elaborated in Table 1.

2.3. Kinetic analysis

For evaluation of heterogeneous esterification kinetic parameters, separate runs were conducted using TED derived optimal condition with varying batch-time; and the corresponding ϕ_{MSN} was evaluated. Furthermore, the amount of MSN formed coupled with other products viz., distearin (DSN) and tristearin (TSN) were quantified by gas chromatograph equipped with DB-wax column (30 m × 0.25 mm × 0.25 μm). The column temperature was preset at 343 K and subsequently increased at a ramping rate of 283 K/min and finally raised to 543 K [21]. The sample injection was split less type with 99.99% helium gas as a carrier (1 ml/min). The MS detector was operated in the EI mode at 70 eV and 40–900 amu.

2.4. Mathematical interpretation

2.4.1. Reaction mechanism

According to the reaction scheme (Eq. (5)), initially, one SA molecule has reacted with one GL molecule to form MSN; which in turn further reacted with another SA molecule to form DSN