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Bottlenecks identification and intensification for transesterification of surplus glycerol and triacylglycerols: Thermodynamics, mechanism and kinetics analysis

Qinli Liu[a,b], Maojian Wang[a,c], Zhao Jiang[a,b], Guidong Yang[a,b], Jinjia Wei[a,b], Tao Fang[a,b,*]

[a] Xi'an Jiaotong University, School of Chemical Engineering and Technology, Xi'an, Shaanxi 710049, PR China
[b] Xi'an Jiaotong University, Shaanxi Key Laboratory of Energy & Chemical Process Intensification, Xi'an, Shaanxi 710049, PR China
[c] Hong Kong University of Science and Technology, Department of Chemical and Biologic Engineering, Clear Water Bay, Kowloon, Hong Kong

HIGHLIGHTS

- A new precise thermodynamics model was proposed and validated by experimental.
- Thermodynamics mechanism among wide-span temperatures was analyzed by proposed model.
- The reaction bottleneck and restriction boundary were identified and proposed.
- The temperature influences over 500 K were conducive for higher MAG yield.
- A series of kinetic experiments for verification were achieved in a catalyst-free system.

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ABSTRACT

Functional monoacylglycerols (MAG) synthesis is an attractive topic not only due to it transforms biofuel industry by-products into high value-added fine chemicals, but also because of abundant applications and large demands of MAG. With efforts for decades, triacylglycerols (TAG) transesterification with glycerol has been experimental studied at a wide temperature range from ambient temperature about 303 K to elevated temperature more than 500 K with various discrete temperatures or small temperature ranges. What's more, the temperature influences on thermodynamics mechanisms of TAG transesterification with glycerol is a crucial issue but regrettably a gap so far. Therefore, in this paper, a new thermodynamics model is proposed for MAG synthesis predictions. To verify its performances, it is compared with four available and reliable models from literatures and further validated by experimental data. As the most suitable and precise one, proposed new model was used for thermodynamics mechanism analysis. The bottleneck of MAG productivity improvement was found as the second step reaction transforming diacylglycerols (DAG) to MAG due to its non -spontaneity in forward direction. The boundary in 500 K was identified and proposed for the first time as potential restriction to increase MAG productivity. The influences of temperature are more pronounced and conducive for high MAG yield at reaction temperature greater than 500 K. Moreover, a series of kinetic experiments of glycerolysis with OFATG at 473 K–533 K achieved rapidly increase of MAG at about 500 K in a catalyst free system, which verified those conclusions from mechanism analysis in front.

1. Introduction

In the last decades, biodiesel has emerged as an alternative fuel in US and in Europe. The global biodiesel production increases to around 30 million tonnes oil equivalent in 2016 [1]. Additional glycerol stemming from biodiesel production is flooding the market. Obviously there is a need to transform glycerol into valuable products. Monoacylglycerols (MAG) synthesis by glycerol is an attractive option to transform this biomass-derived compound into fine chemicals [2,3].

MAG is ubiquitous in plants and animals and has various applications in numerous industries [4–6], which account for approximately 75% of the world's annual emulsifier production [3,7–9]. MAG is widely used as food-grade additives [10–12], drug carriers [13], modifiers and synthetic intermediates [14]. In addition, many kinds of

* Corresponding author at: Xi'an Jiaotong University, School of Chemical Engineering and Technology, Xi'an, Shaanxi 710049, PR China.
E-mail address: taofang@mail.xjtu.edu.cn (T. Fang).

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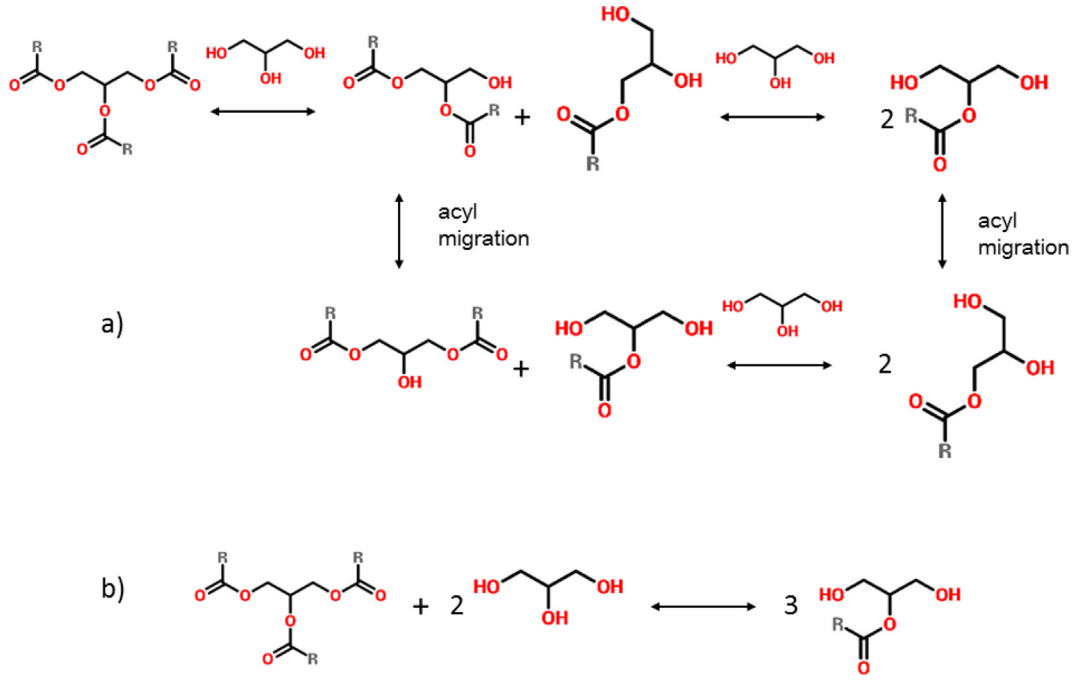

Fig. 1. Reaction schemes for MAGs production. a) two step reversible reaction in details; b) overall simplified reaction. R, fatty acid chain.

mono-unsaturated and poly-unsaturated MAG have positive effects on human health such as preventing prostatic hyperplasia or cardiovascular disorders [15]. Due to the progressive increase in production of glycerol, MAG have become and will be still one of such bio-products.

Based on industry practices, MAG are commercially produced by glycerolysis of triacylglycerols (TAG) at high temperatures as shown in Fig. 1. Alkali catalysts, such as NaOH, KOH, and $Ca(OH)_2$, are usually used to accelerate the process. However, the MAG yield is usually stopped at rather low level about 30–40% at the end of the reaction time [16]. As a result, an energy-intensive molecular distillation is always occupied to purify these preliminary products, in order to obtain high-quality product with at least 90% MAG. But this additional separation process severely increases the overall production cost. Thus, there is an urgent requirement to improve TAG glycerolysis reactions to enhance MAG productivity. During the past decade, extensive researches have been carried out. To intensify MAG productivity for TAG glycerolysis reactions, amount of experimental works have taken and published in different temperature conditions.

In the literature, plenty of glycerolysis reactions were conducted in various discrete temperatures. Enzymatic glycerolysis usually carry out at mild conditions with temperature below 353 K [15,17–19]. For examples, Cheirsilp et al. conducted reaction with an alginate immobilized lipase at 303 K and achieved MAG yield of 54% [20]. What's more, Damstrup carried out glycerolysis reaction at 323 K with kinds of organic solvent [21]. While Baum synthesized MAG at 338 K in 5 wt% amphoteric surfactant cocamidopropyl betaine [22].With temperature going up, chemical catalysts other than enzyme are frequently used to assist glycerolysis reactions. Sutter et al. firstly conducted glycerolysis of triolein with BaO (22%)/Al_2O_3 (78%) at 393 K and MAG yield reached 7% after 24 h. After that, triolein glycerolysis reactions with CaO, K_2CO_3 and BaO (22%)/ Al_2O_3 (78%) were conducted respectively at 473 K. While MAG yields had been achieved from 51% to 68% after 48 h for those reactions [23]. At the same temperature as 473 K, Zhang et al. reported MAG yield reached 46.8 wt% in the acylglycerol phase with K_2CO_3/HT after 2 h [24]. What's more, Ferretti et al. synthesized MAG with MgO as basic catalyst and obtained 38% MAG yield at 493 K [25]. And Ong et al. proposed a novel CuO-nano/NaOH catalyst system to help MAG yield to improve to 71% at 513 K [26].

Besides that, some literatures studied glycerolysis reactions in small temperature ranges in terms of MAG yield. Remonatto et al. studied glycerolysis using Novozym 435 enzyme at 313 K–343 K and obtained 65 wt% of DAG + MAG yield at 343 K [27]. Keskin et al. synthesized 2-MAG by six lipases at 318 K–333 K and obtained the best MAG yield at 318 K after 5 h [28]. Moreover, Luo et al. have explored the MAG synthesis with 1-Butyl-3-methylimidazolium imidazolide in the temperature range from 443 K to 473 K. They concluded that selectivity to MAG greatly increased with temperature from 443 K to 473 K. The highest MAG yield has been obtained at 473 K with the value of 65% [29].

The literature investigation indicated that MAG production through glycerolysis could be achieved in a wide temperature range from ambient temperature about 303 K to elevated temperature more than 500 K. However, there are still a lot of blank fields without explorations among that large temperature range. Since enzymatic glycerolysis usually conducted lower 353 K, while chemical catalyst assisted MAG synthesis are almost studied at temperature higher than 473 K. Even for the temperature region below 353 K and beyond 473 K, only discrete temperatures and small temperature intervals have been explored so far. Therefore, for the temperature influences on glycerol transesterification with TAG in terms of MAG yield, there are three essential questions needed to be answered:

1. Whether temperature has any influence on TAG glycerolysis reactions or not, especially in the regions without existing experimental data?
2. If there are influences, whether those influences keep the same or change different among large temperature range from ambient to elevated temperature or not?
3. If those influences change, which temperature should be suggested for MAG production? Ambient or elevated one? Is there any specific guideline?

To answer those questions, the explorations should be focus on quantitative thermodynamics analysis since detailed kinetics mechanism varied too much in large temperature range for TAG glycerolysis reactions. As we all know, the equilibrium positions in certain reaction system are determined only by interactions among reactants and products. While the nature and behavior of any catalyst (either