

Comparison study of plug flow and batch reactors for the reaction of glycerol with tert-butanol catalyzed over Amberlyst-70

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Abstract

The reaction of glycerol with tert-butanol (TBA) on the sulfonated carbon catalyst (Amberlyst-70) was carried out in a plug flow and batch reactor for producing value added products, gasoline and diesel fuels additives. The reaction was performed under the temperatures ranged from 160°C to 190°C and the pressure ranged from 50atm to 70atm. The results showed that the conversion of glycerol to react with TBA in the plug flow system was significantly decreased from 100% to 70% within 4hr. This reaction was based a molar ratio of TBA to glycerol of 4:1 in the flow rate of 0.5mL/min or weight hour space velocity (WHSV=1.2h⁻¹) at the pressure of 50atm and temperature of 180 °C . Meanwhile, no tri-butyloxy glycerol ether (TBGE) and low boiling point hydrocarbons (HCs) was found in plug flow reactor. On the contrary, they were found in the batch reactor, and the catalyst decade was slight to compare with the plug flow reactor. There is possible reason for the active sites of A-70 catalysts, sulfonated group, rapidly leached away by the flow stream of reactant and product during the reaction. Finally, the product mixtures was cooled down directly separating into oil phase (including TBGE and HCs) and water phase (including glycerol) at reaction temperature > 180°C in batch reactor. A high octane number (>100) of distilled oil was obtained from simple distillation at 225°C . It could be a candidate of fuel additive for gasoline (bio or petroleum). The composition of products were also analyzed by GC/MS and quantified by GC and Karl Fisher.

Keywords: glycerol, tert-butanol, fixed bed reactor, oxygenated additive.

1 Introduction

Biodiesel has been recognized to be potential alternative renewable fuels in the future world. It is a clean-burning diesel fuel generated from renewable resources, while glycerol is a major byproduct in the biodiesel manufacturing process. In general, for every 100 pounds of biodiesel produced, approximately 10 pounds of crude glycerol are created. With the rapid expansion of the biodiesel industry, an excessive amount of crude glycerol is being created, with the result that in the corresponding downtrend in the price of crude glycerol makes the by-product (glycerol) an attractive platform chemical. A number of value-added products derived from glycerol have already been proposed, and some of them are commercialized.[1-4]

It is a possible way for the upgrade of glycerol to oxygenate as fuel additives for both gasoline and diesel by transform it into higher ethers. The gasoline oxygenates are added to enhance the octane rating of internal combustion engines and to reduce air pollution by ensuring a more complete fuel combustion in the engines. Meanwhile, the use of oxygenated compounds with diesel is designed to reduce harmful exhaust emissions, namely particulates, and sometimes NO_x as well.[5] The etherification of glycerol with methanol to produce glycerol mono-methoxy ethers (GMMEs), di-methoxy ethers (GDMEs) and tri-methoxy ether (GTME) as a green solvent can be found in the works of García et al. and Chang et al.[6,7] The production of the mixture of GDMEs and GTME as an oxygenate additive is promising[4,7-11] because the feedstock of methanol is much cheaper than that of isobutylene or tert-butyl alcohol.

Di- and tri-tert-butyl ethers of glycerol with a high content of di-ethers produced by the etherification of glycerol with

isobutylene (IB) or tert-butyl alcohol (TBA) using homogeneous or solid acid catalysts have been considered promising as oxygenate additives for diesel fuels.[1,12,13,15-18] There are many research papers addressing the etherification of glycerol with isobutylene or tert-butyl alcohol on solid catalysts[1,12-17] to produce a desired oxygenate. A summary of the operating conditions of the relevant literatures is provided in our previous study [19]. It is not included for adopting homogeneous catalysts such as p-toluenesulfonic acid or phosphorustungstic acid, because of the known technical problems and environmental reasons. For the heterogeneous catalysts, low reaction temperature (below 100°C) and low yields of DBGEs and TBGE were found in the main features of the etherification of glycerol with IB or TBA. However, Lee et al. showed that the yields of DBGEs and TBGE can be improved using partial exchange of acidic protons of the adopted solid acid (Amberlyst-15) with suitable metal cations.[1] In a designed TBA etherification plant, the di-, triethers and water were removed from the homogeneous product mixtures while the monoether and unconverted reactants (glycerol and TBA) were recycled to the reactor.[20] However, the separation of di-ethers and tri-ethers from water requires a fine distillation at very high operation cost. In our previous work, different features were noticed. The product mixture was automatically separated into an organic phase and an aqueous phase when the reaction of glycerol with TBA was carried out at elevated temperatures (above 170 °C). Furthermore, the components in the organic phase can be tailored to a diesel-like fuel by a simple distillation. These features motivated us to try catalyst, a high temperature resistance, A-70 and investigate its reaction behavior. Reactions kinetic of plug flow and batch reactors are compared in this work.

2 Experimental

2.1. Material preparation

The catalyst A-70 was purchased from Dow chemical company further dried at 110°C in an oven before the reaction. Structure of sulfonated group of catalyst was shown in Figure 1. Glycerol (99%) and TBA(99%) were obtained from Sigma-Aldrich. All the chemicals and

solvents were analytical grade purity.

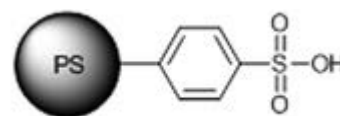


Figure 1 sulfonated group catalyst of A-70

2.2. Reaction system

In this study, two type of reactor systems were used to carry out the reaction of glycerol with TBA. For the plug flow reactor system, it was shown Figure 2. The feed stock of glycerol mixing with TBA (based on molar ratio of 1:4) was carried out in a plug flow reactor packing with 20g dried catalyst. Each unit of the equipment is indicated as following: (1) feed stock bottle, (2) pump, (3) thermal couple, (4) gauge, (5) heating, (6) catalyst bed, (7) packing bed, (8) back pressure regulator (9) sampling output.

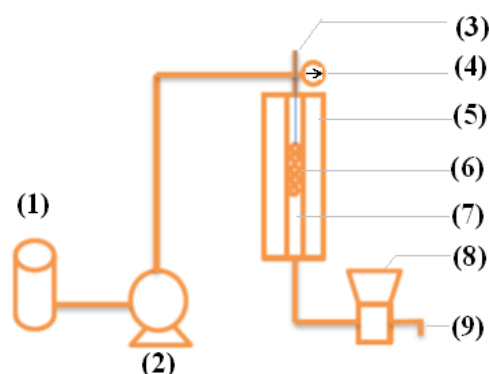


Figure 2. Plug flow reactor system

For the batch type reactor system, the reactions of glycerol with TBA were carried out in a 500 cm³ stainless steel “jacketed-batch reactor” with magnetic stirrer. The batch type reactor system is shown in Figure 3. Each unit of the equipment is indicated as following: (1)nitrogen bottle, (2) valve, (3) stirrer, (4) shaft seal, (5) gauge, (6) catalyst, (7) heating, (8) timer, (9) controller.

2.3. Experimental condition and procedure.

The different experimental procedures are respectively described for plug flow and batch reactors as below: For plug flow reactor, the feed stocks were prepared by mixing a well-defined molar ratio (1:4) of glycerol and TBA, and

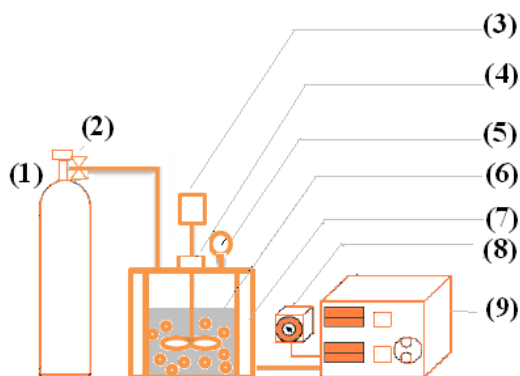


Figure 3 Batch reactor system

dry solid catalyst (A-70) suitable amount (1-20g) were loaded into the plug flow reactor with fixed bed form and heated up to a prefixed reaction temperature in 10 min. Then, the feed stock was continuously pumped with a suitable WHSV into the plug flow reactor for carried out the reaction. The reaction was controlled at the pressure of 50atm and temperature ranging from 120 to 180°C. Then, the product mixtures from output of reactor were cooled down down to 5°C by an ice-bath and divided into gas and liquid phases form in room temperature. Finally, the product liquid mixture was separated into an organic phase and an aqueous phase automatically after cooling and settling. It will play an incentive role in the process development because the cost of separation will be minimized. The organic phase product was further analyzed by GC.

For batch reaction, the experimental procedures described below were followed: a well-defined amount of glycerol, TBA, and dry solid catalyst (A-70) were first loaded into the batch reactor and heated up to a prefixed reaction temperature in 10 min. Before heating up the reactor, the reactor was fluxed with nitrogen to remove the air. Then, the reactor was cooled down to 5°C by an ice-bath until the vapor pressure of the mixture turned down to the atmospheric one, thus allowing all the condensable gas phase compounds to condense back to the liquid phase mixture. The product mixture was separated into an organic phase and an aqueous phase automatically after cooling and settling. The product analysis was described as below section.

2.4. Product Analysis.

A gas chromatograph (Techcomp Shanghai Ltd. Co.) GC7900, which was provided with a capillary column Varian CP9210 (l, 30 m; i.d., 0.32 mm; film thickness, 0.5 mm) under the oven temperature programed from 40 to 250 °C (with a heating rate of 10°C min⁻¹) and at 250°C for 3 min, analyzed the manually injected samples (0.2 μl) of the reaction product. Each data set was obtained with an accuracy of ±3% from an average of three independent measurements, using the internal standard method (n-butanol, 2 wt.% in respect to the sample). Water content was measured with the Karl Fisher Titrator, MKS-500. For quantification of the reaction product, the standards (DIBs and TIBs) were purchased from Alfa Aesar and TCI.

2.5 Reaction mechanism

Glycerol has three hydroxides group to carried out, SN2 replacement, the etherification reaction with TBA alcohol. The possible reaction pathway for the reaction of glycerol with TBA was shown in Figure 4.

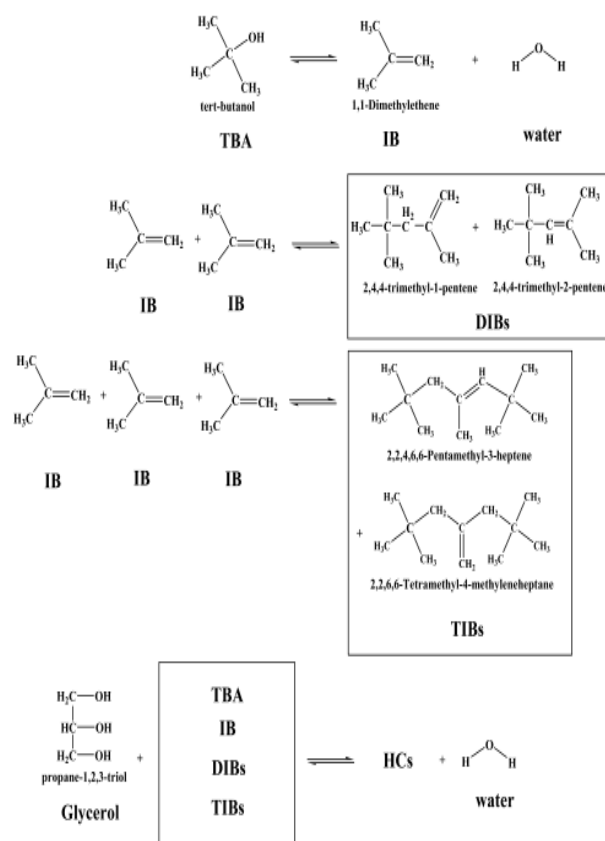


Figure 4. The possible reaction pathway for the reaction of glycerol with TBA[19]

3 Results and Discussion

3.1. Temperature effect.

The reaction of glycerol with TBA was studied by adopting A70 as a solid acid, experiments were carried out at different temperatures 120, 150, and 180°C with the feed speed with WHSV=1.2 at pressures of 50atm. GC spectra of the products were shown in Figure 5. For temperature, the reaction products of the plug flow reactor are similar with that of batch reactor.

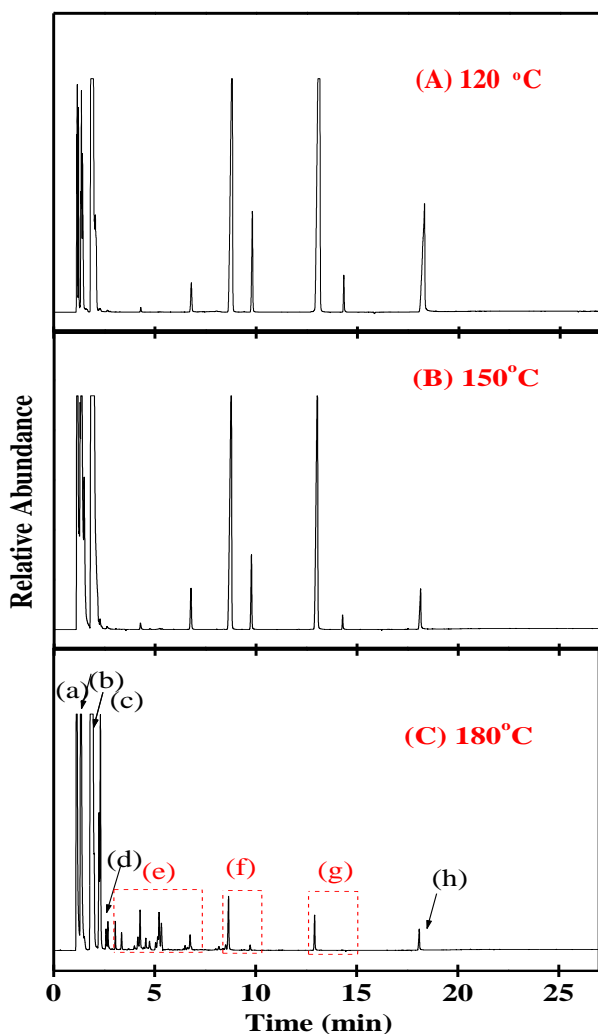


Figure 5. GC spectra of the output products (organic phase) from reaction at different temperatures (120, 150, 180°C) and WHSV=1.2hr⁻¹.

Each component is indicated as following: (a) isobutylene (IB) ,2,2,4-trimethyl-1-pentene, (b) 2,4,4- trimethyl-2-pentene (DIBs), 2,2,4,6-pentamethyl-3-heptene, (c) TBA (d) 2,2,6,6-tetramethyl-4-methyleneheptane (TIBs) (e) TBGE and its isomers (f) DBGE and its isomer and HC (g)

MBGE and its isomer (h) glycerol. It is indicated that the more TBGE produces at the higher temperature. Moreover, there are also found some oxygen-limited hydrocarbons (HCs) at higher temperature.

3.2. Catalyst deactivation.

For plug flow reactor, the deactivation was observed in Figure 6. The reaction of glycerol with TBA was studied at temperatures of 180 °C with the feed speed with WHSV=1.2 at pressures of 50atm. The conversion of glycerol was obviously found. For batch reactor, the deactivation of A-70 was also found about 20% decrease for each run at 170°C based on the amount of catalyst/initial reactant=8wt% for 8hr.

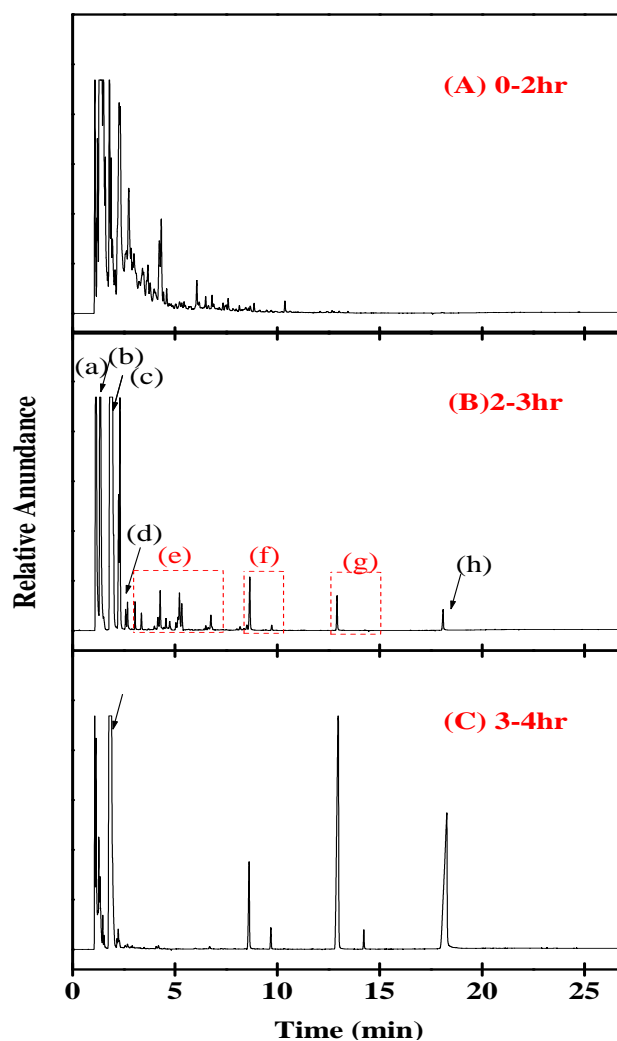


Figure 6. GC spectra of the output products dependent on reaction time for plug flow reactor at 180°C and WHSV=1.2hr⁻¹.

3.3. Comparison analysis.

To compare with commercial diesel oil and gasoline, the distilled oil phase product was further analyzed by using GC as shown in Figure 7. Some component has been identified such as IB, DIB, TAB, TIB as Figure 5, but others are not identified in region I. The region II and region III are similar, respectively, with (f) and (g) in Figure 5.

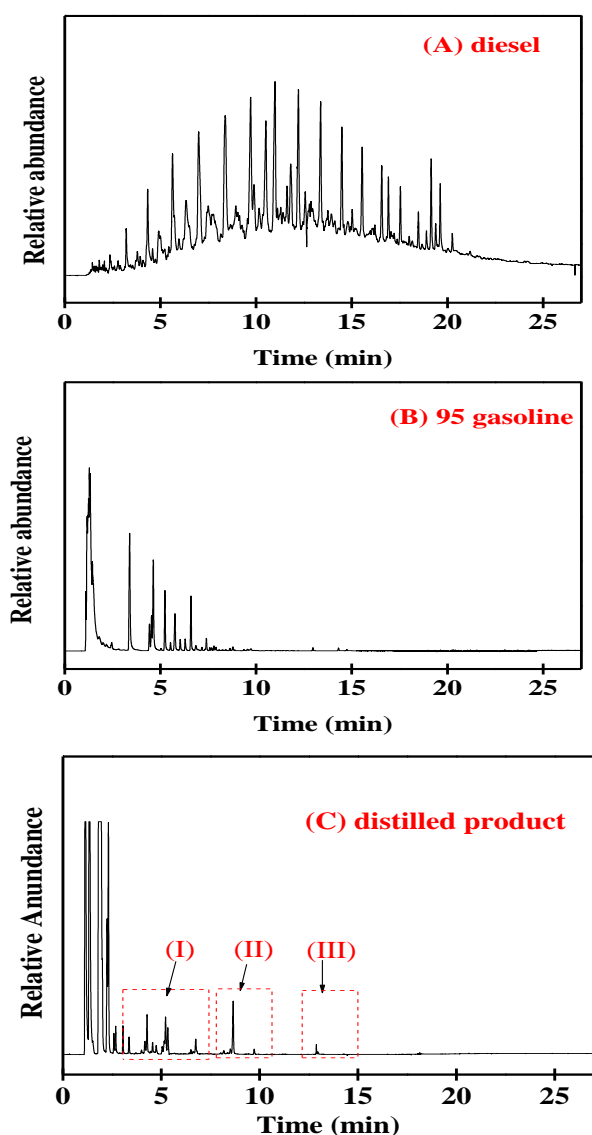


Figure 7. GC spectra of (A) commercial diesel (B) gasoline and (C) the products reacted at temperatures of 180°C organic phase products.

For the unknown components of distilled oil phase product at 225°C, we call them as HCs which are possibly formed from the reactions (including: etherification, dehydration or isomerization) of glycerol with TBA.

However, HCs could also be separated by distillation at suitable temperature. To identify the unknown HCs, some standard compounds are needed to make conformation. For composition analysis, the component of distilled or undistilled oil phase product was analyzed by GC as shown in Figure 7(C). The distilled oil phase product only not found IB and glycerol, because of IB with low boiling point and glycerol with high boiling point. Thus, most of them could be removed after distillation at 225°C. The distilled oil phase product was collected by simple distillation method at 225°C.

3.4. Fuel property analysis.

To compare with diesel, the cetane index for the oil phase product was estimated by adding 10wt% amount into diesel oil as shown in Table 1. Cetane index(CI) of distilled oil phase product, respectively, were 52.4 larger than original diesel 51. This oil phase product could be calculated as 65 and used as diesel like additive. For gasoline, octane number of distilled oil phase product larger than 100 was analyzed as Table 2. It is good octane booster for engine fuel.

Table 1. properties of cetane index of undistilled oil phase product

Analyst	CI
Diesel(CPC)	51
Diesel added with 10wt% undistilled oil product	52.4
Distillation oil product	65*

*: calculated by proportional method

Table 2. properties of octane number of distilled oil phase product at 225°C

Analyst	ON
95 gasoline(CPC)	95
Distillation oil product	>100

4 Conclusion

The reaction behavior of glycerol with tert-butanol on the sulfonated carbon catalyst (A-70) was studied in plug flow and batch reactors at different temperatures 120, 150, 180°C. For both plug flow and batch reactors, a

homogeneous phase of the product was similarly found when the reaction temperature controlled at 120 and 150°C. At the temperature of 180°C, a separation phase (oil/water) was appearing. At the temperature of 180°C, phase segregation was significantly observed. The deactivation in plug flow reactor is more serious than that in batch reactor. For fuel properties, CI of undistilled oil phase product is 65 and octane number of distilled oil phase product at 225°C is larger than 100. It could be octane booster for gasoline.

Acknowledgments

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