Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

INVESTIGATION OF MASS TRANSFER LIMITATIONS IN SIMULTANEOUS ESTERIFICATION AND TRANSESTERIFICATION REACTION USING HETEROGENEOUS CATALYST

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a)

$$FFA + Methanol \leftrightarrow Biodiesel + Water$$

b)

$$TG + Methanol \leftrightarrow DG + Biodiesel$$

$$DG + Methanol \leftrightarrow MG + Biodiesel$$

$$MG + Methanol \leftrightarrow Glycerol + Biodiesel$$

Figure S1. Reaction schemes for a) esterification reaction and b) step-wise transesterification reaction.

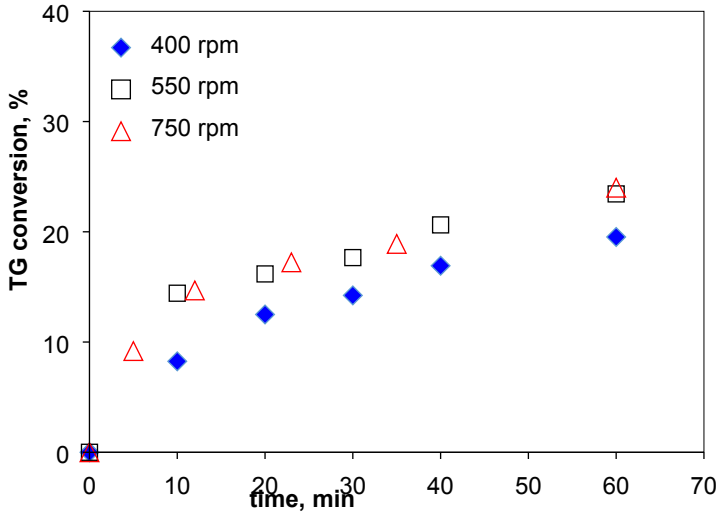

Figure S2: Effect of agitation speed on TG conversion in spinning basket reactor. Temperature: 170 ºC, Methanol to oil molar ratio 6:1, Catalyst loading: 0.083 w/w.

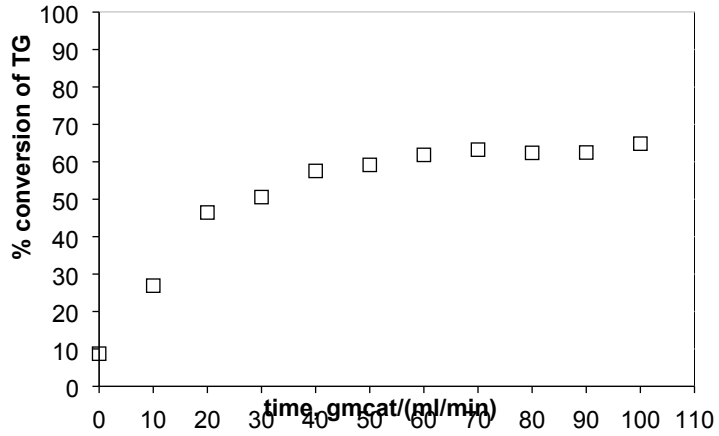

Figure S3: TG conversion in spinning basket reactor, methanol to oil molar ratio-6:1, Temperature: 200 ^{o}C

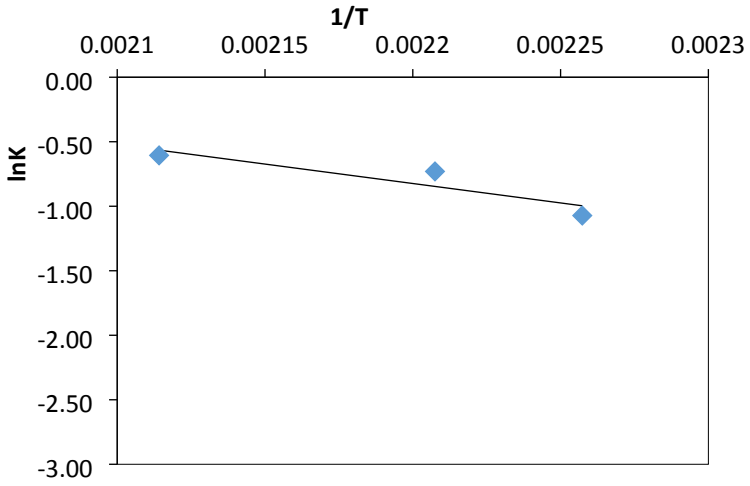

Figure S4:: Activation energy plot

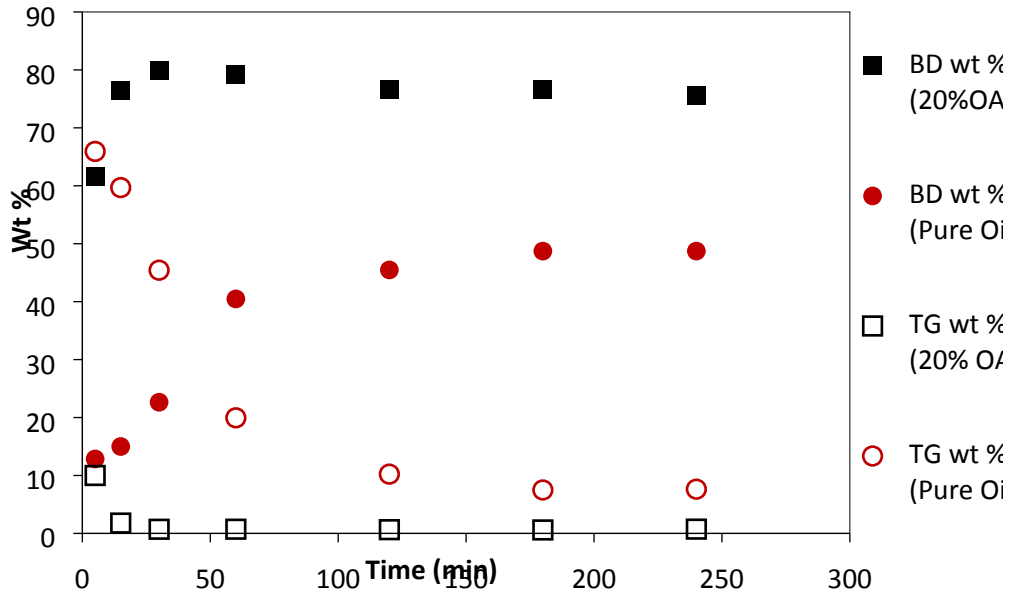

Figure S5: Equilibrium and kinetics in the presence and absence of FFA in sunflower oil

(Conditions: Temperature 200 C; Catalyst loading 0.5 wt%; RPM 800; methanol to oil (mixture) mole ratio 1:6)

Proposed process using heterogeneous catalyst

Figure S6 illustrates the conventional process which uses two steps *viz*. esterification followed by transesterification. The feedstock is *Jatropha* oil containing 20 % (w/w) FFA and catalyst used is homogeneous (H_2SO_4 for esterification and NaOH/KOH for transesterification). In the first step, FFA is reacted with methanol to give biodiesel. This is an acid catalyzed reaction wherein, H_2SO_4 is generally used as a catalyst. The product mixture is then separated in two phases. The top layer containing acid, methanol and water is sent to the neutralization stage wherein the acid is neutralized. Further, methanol is recovered from water by distillation and recycled. The bottom layer from the decanter is sent to the transesterification reactor wherein, it reacts with methanol in the presence of KOH as a catalyst. After transesterification, the product mixture is separated in two phases. The top layer contains unreacted oil, biodiesel, methanol and KOH. Methanol is removed by atmospheric distillation and KOH is removed by water wash. During water washing substantial amount of biodiesel is lost thereby reducing the overall yield of biodiesel. This layer containing unreacted oil and biodiesel is then subjected to

vacuum distillation to obtain pure biodiesel. The bottom layer of decanter, containing glycerol, methanol and KOH, is then acid treated to neutralize KOH, followed by methanol recovery, to obtain pure glycerol. There are several post-reaction steps in homogeneous process and they also result in a loss of the product(s). In the process with homogeneous catalyst, the reactor is operated close to methanol boiling temperature (~60 °C) and at atmospheric pressure.

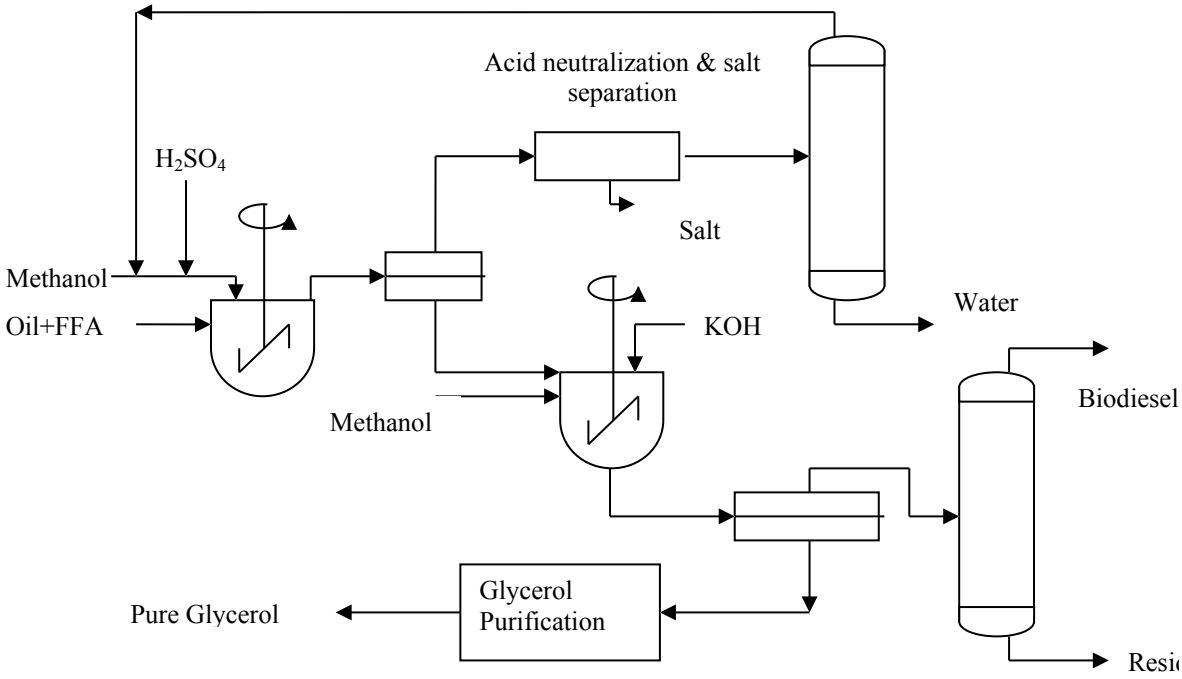

Fig. S6. Two stage homogeneous process flow diagram

Figure S7 shows the flow diagram of the proposed continuous process that uses heterogeneous catalyst. The typical operating conditions, based on the present study, for heterogeneous process are: temperature 170-200 °C and pressure 40-60 bar. The preheated feed (*jatropha* oil containing 20% (w/w) FFA) is fed to the fixed bed reactor 1. The reactor is packed with ZnO/ZSM-5 pellets. The reaction mixture from reactor 1 is cooled, decanted and the biodiesel layer containing unreacted oil is sent to the fixed bed reactor 2 for subsequent reaction to improve the yield of biodiesel. Further, from reactor-2, after methanol removal, the biodiesel layer containing unreacted oil is sent to distillation column to obtain biodiesel as a pure product. Glycerol layer containing methanol from both the columns is sent to a flash drum (or stripper) wherein, methanol is recovered and recycled. In this process, glycerol is obtained as a pure byproduct. Thus with the help of catalyst developed in this study, the complexity of the homogeneous process can be reduced significantly. The Esterfip-H technology, developed by

French Institute of Petroleum, has proposed a similar flowsheet for their heterogeneous catalyst for production of biodiesel on a commercial scale.[1]

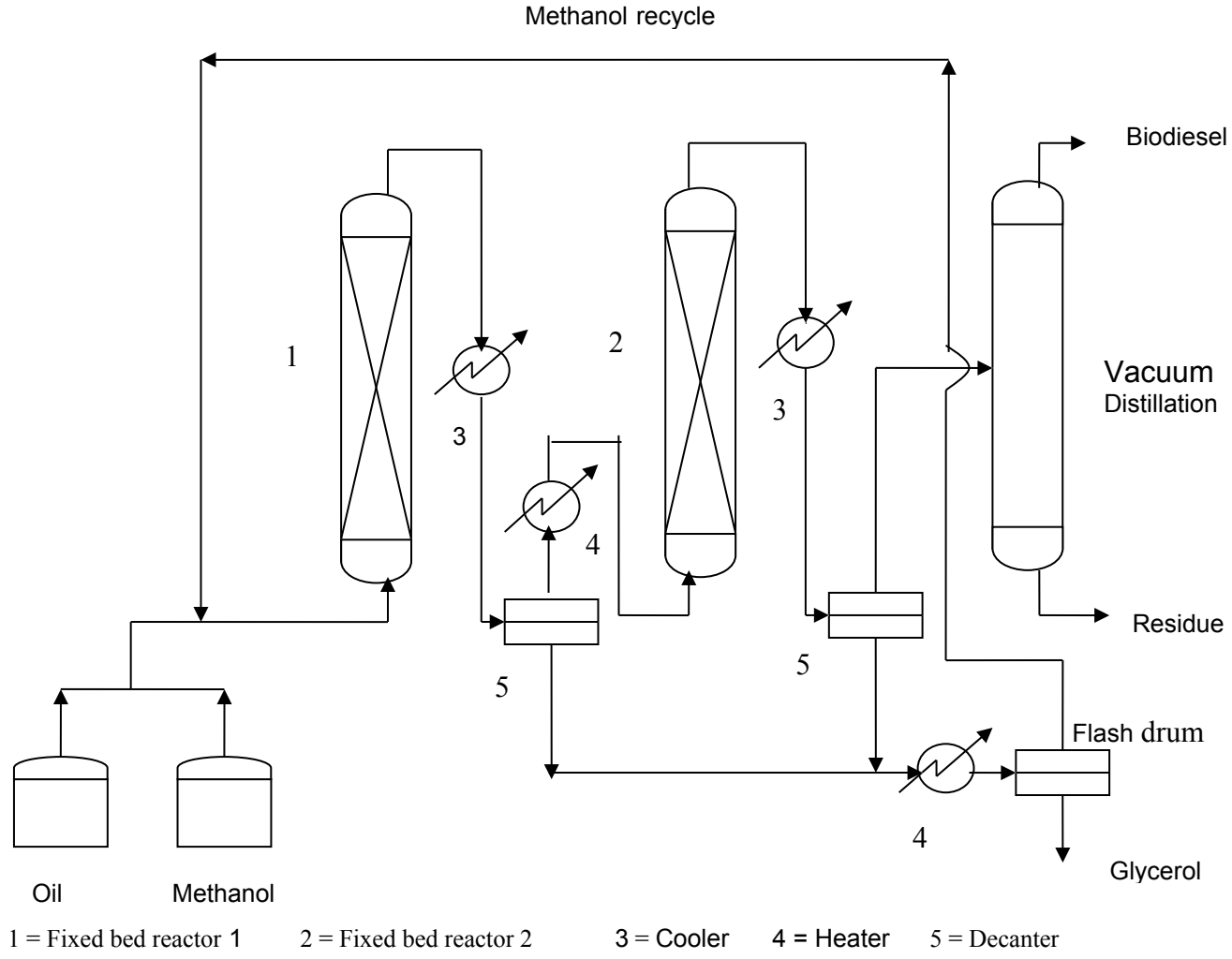

Fig. S7. Conceptual design of the proposed process with heterogeneous catalyst.

Reference:

1. Bournay, L.; Casanave, D.; Delfort, B.; Hillion, G.; Chodorge, J. A. New heterogeneous process for biodiesel production: A way to improve the quality and the value of the crude glycerin produced by biodiesel plants. *Catal. Today* **2005**, *106*, 190.