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Article · August 2013

DOI: 10.1109/ICMREE.2013.6893646

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Simulation of the Catalytic Reactive Distillation Process for Biodiesel Production via Transesterification

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***Abstract*—In order to simulate catalytic reactive distillation process for biodiesel production via transesterification accurately, the Antoine parameters of biodiesel and NRTL binary interaction coefficients were regressed using Aspen Plus Data Regression function according to the data in literatures. Then vapor pressure of biodiesel under different temperature and phase equilibrium conditions could be described with these parameters. Catalytic reactive distillation process for biodiesel production via transesterification was simulated with Aspen Plus software successfully. Reaction and separation was integrated in one catalytic reactive distillation column. As a result, although methanol-to-oil ratio was only 4:1, high purity (99.8 wt %) of biodiesel with high yield (99.7%) was obtained. The catalytic reactive distillation process for biodiesel production via transesterification would be adequately good to have a potential industrial relevance.**

Keywords—Simulation, Catalytic Reactive Distillation Process, Biodiesel Production, Transesterification, Aspen Plus

I. INTRODUCTION

Biofuels, along with solar, wind and tide energy, plays an important role in the energy consumption. As a kind of biofuels, biodiesel is usually produced via transesterififcation of vegetable oil or animal fat with methanol, which is catalyzed by acid or base catalysts. The homogeneous catalysts such as H_2SO_4, H_3PO_4, KOH and NaOH have been used in the biodiesel industries for decades [1] [2]. However, the homogeneous catalysts result in neutralization operation, waste water and equipment corrosion problems. In order to overcome these shortcomings, lots of heterogeneous catalysts including zeolites, heteropoly acids, functionalized zirconia and silica, basic zeolites, hydrotalcites, alkaline earth oxide base and alkaline metal salt on porous support were employed [3] [4] [5].

Catalytic distillation process is a method for conducting chemical reactions and separating the reaction mixtures in one column. Catalytic reactive distillation for biodiesel production is attractive for both economical and ecological reasons. Some researchers have developed catalytic reactive distillation for biodiesel production via esterification, in which fatty acid was feed on the top of the catalytic reactive column, and methanol was feed on the bottom of the catalytic reactive column as vapor. With the solid catalyst packed in the catalytic reactive column, esterification occurred and biodiesel was pumped from the bottom while water by-product was distillated from the top. Kiss et al. [6] [7] [8] analyzed the feasibility of catalytic reactive distillation for biodiesel production, simulated the process using Aspen Plus software and proposed a new thermally coupled catalytic reactive distillation process for biodiesel. They concluded that the catalytic reactive distillation process improved efficiency and considerably reduced the energy requirements for biodiesel production. Machado et al. [9] simulated fatty acid esterification in reactive distillation columns, higher conversion and lower energy consumption were obtained.

More researches about catalytic reactive distillation process via transesterification instead of esterification should be done because esterification is just a pretreatment of the whole biodiesel production. In addition, it will reduce the excess methanol if we fulfill catalytic reactive distillation process via transesterification. Da Silva et al. [10] and He et al. [11] achieved catalytic reactive distillation process via transesterification experimentally. Regretfully, the catalysts they use were still homogeneous.

The current work presents simulation case study of the catalytic reactive distillation process for biodiesel production via rransesterification using our own heterogeneous catalytic kinetics. Aspen Plus software was employed to simulate the catalytic reactive distillation process.

II. METHODOLOGY

A. Pure Components Properties

Four pure components were used in this simulation. As both vegetable oil and biodiesel are complicated mixtures, triolein ($C_{57}H_{104}O_6$) and methyl-oleate ($C_{19}H_{36}O_2$) were used to represent vegetable oil and biodiesel, respectively. All pure component properties except Antoine parameters of biodiesel came from Aspen Plus software database. Boiling points of biodiesel under different pressure were determined using the method proposed in the literature [12]. Then Antoine parameters of biodiesel were regressed using Aspen Plus's data regression function according to calculated vapor pressure data.

B. Thermodynamic Model and Phase Equilibrium Data

In the biodiesel production system, both polar and non-polar substances exist. Therefore, ideal thermodynamic models may not be suitable for this system. By contrast, after binary interaction coefficients were regressed on the basis of vapor-liquid and liquid-liquid phase equilibrium dada in the literature [13], NRTL

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(non-random of two liquids) model could describe the thermodynamic phenomenon exactly.

C. *Process Simulation Specifications*

The catalytic reactive distillation process for biodiesel production via transesterification is simple. Vegetable oil and methanol, heated to specific temperature, were pumped into a catalytic reactive distillation column in which a designed cylinder shape solid catalyst was packed. All excess methanols was distilled out of the column from the top while biodiesel and glycerol mixture were pumped out of the column from the bottom. The mixture was cooled down and separated into two phases. One phase was biodiesel product and the other was glycerol by-product. The RadFrac model in Aspen Plus was used to simulate the catalytic reactive distillation column. It is a rigorous distillation model including material balance, energy balance, phase equilibrium and reaction rates on each stage.

A 30000 ton biodiesel production per year was simulation using RadFrac model in Aspen Plus software. The kinetic data was from our previous work [14]. Other specifications of the column were listed in TABLE I.

TABLE I. COLUMN SPECIFICATIONS

	Units	Value
Stages in Total		20
Oil Feed Stage		6
Methanol Feed Stage		15
Distillate Rate	kg/hr	151
Reflux Ratio		4.2
Pressure	mmHg	100

III. RESULTS AND DISCUSSION

A. *Pure Components Properties Results*

Some basic properties of the four main components are listed in TABLE II.

TABLE II. PURE COMPONENTS PROPERTIES LIST

	Units	$C_{19}H_{36}O_2$	$C_{57}H_{104}O_6$	CH_4O	$C_3H_8O_3$
Freeze point	C	19.90	5.00	-97.68	18.18
Molecular weight		296.49	885.45	32.04	92.09
Pitzer acentric factor		1.05	1.21	0.57	0.51
Critical pressure	MPa	1.28	0.47	8.08	7.50
Normal boiling point	C	343.85	846.85	64.70	287.85
Critical temperature	C	490.85	1366.85	239.35	576.85
Critical volume	cum/kmol	1.06	3.09	0.12	0.26
Critical compressibility factor		0.21	0.11	0.22	0.28

All properties in the list agreed with the data from NIST database.

The biodiesel production needs to be refined by vacuum distillation. Therefore, the boiling points of biodiesel under different pressure or the vapor pressure of biodiesel under different temperature were very important so that the simulation can be accurate. Figure 1 showed our regressed data compared with the data from literature [12].

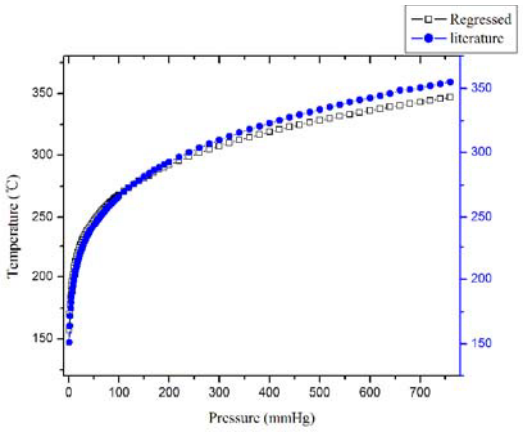

Figure 1. Vapor pressure of biodiesel regressed data compared with data from literature

From Fig.1 we can see that under vacuum conditions (1-100 mmHg) the regressed data agreed well with the literature data and the differences was less than 1%.

B. *Ternary Phase Map*

After the transesterification reaction, nearly all vegetable oil converted into biodiesel and glycerol. A mixture of methanol, biodiesel and glycerol was obtained. To describe the phase equilibrium, we also regressed the binary interaction coefficients of methanol, biodiesel and glycerol using phase equilibrium dada [13]. Figure 2 showed the Ternary Phase Map which was consistent with the data reported previously.

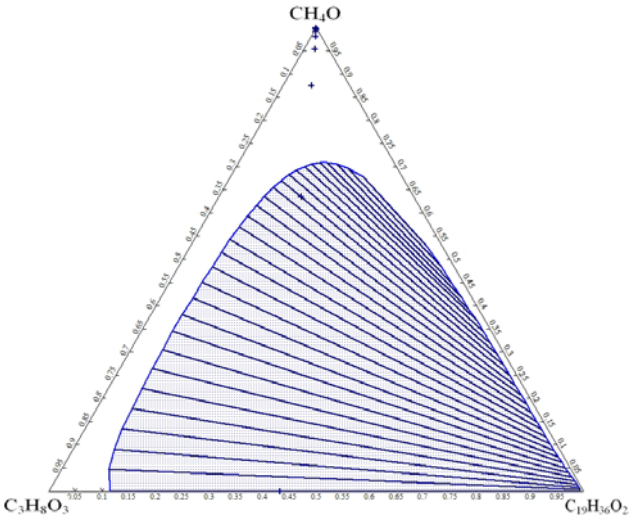

Figure 2. Ternary Phase Map of Methanol, Biodiesel and Glycerol at 25℃

C. *Process Simulation Flowsheet and steams Results*

Figure 3 showed the flowsheet of catalytic reactive distillation process for biodiesel production via transesterification. Reaction and separation was integrated in one catalytic reactive distillation column. Vegetable oil was pumped into the column with a flow rate of 4166.7

kg/h and methanol was pumped into the column with a flow rate of 603 kg/h (Methanol-to-oil ratio was 4:1). Biodiesel with a flow rate of 4170.1 kg/h was obtained and the purity was 99.8 wt%. Glycerol with a flow rate of 431.1 kg/h was obtained and the purity was 98.3 wt%. Main steams results were listed in TABLE III. Although methanol-to-oil ratio was only 4:1, high purity (99.8% wt) of biodiesel with high yield (99.7%) was obtained.

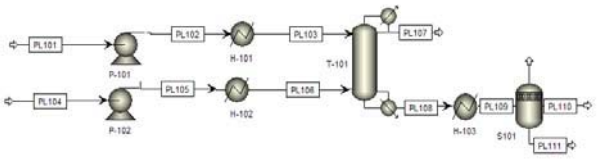

Figure 3. Ternary Phase Map of Methanol, Biodiesel and Glycerol at 25℃

TABLE III. MAIN STEAMS RESULTS

Stream Name	PL101	PL104	PL107	PL110	PL111
Mole Flow kmol/hr					
$C_{19}H_{36}O_2$	0.00	0.00	0.00	14.06	0.02
$C_{57}H_{104}O_6$	4.71	0.00	0.00	0.01	0.00
CH_4O	0.00	18.82	4.71	0.01	0.01
$C_3H_8O_3$	0.00	0.00	0.00	0.01	4.68
Mass Flow kg/hr					
$C_{19}H_{36}O_2$	0.00	0.00	0.00	4170.09	6.92
$C_{57}H_{104}O_6$	4166.70	0.00	0.00	8.54	0.08
CH_4O	0.00	603.00	151.00	0.23	0.36
$C_3H_8O_3$	0.00	0.00	0.00	1.33	431.15
Mass Frac %					
$C_{19}H_{36}O_2$	0.00	0.00	0.00	99.76	1.58
$C_{57}H_{104}O_6$	100.00	0.00	0.00	0.23	0.05
CH_4O	0.00	100.00	100.00	0.00	0.05
$C_3H_8O_3$	0.00	0.00	0.00	0.01	98.32
Total Flow kg/hr	4166.70	603.00	151.00	4180.19	438.51
Temperature C	20.00	20.00	20.63	25.00	25.00
Density kg/cum	909.27	798.84	798.09	868.61	1259.26
Average MW	885.45	32.04	32.04	296.56	92.98

D. Process Simulation Catalytic Reactive Distillation Results

Proper pressure reduction (100 mmHg) was needed to keep the reboiler temperature lower than 200 ℃ and condenser temperature higher than 20℃. The temperature profiles of the catalytic reactive distillation column were showed in Figure 4 in which temperature evenly distributed from the top to the bottom.

Liquid compositions profiles and reaction extend profiles of the catalytic reactive distillation column were showed in Figure 5 and Figure 6, respectively.

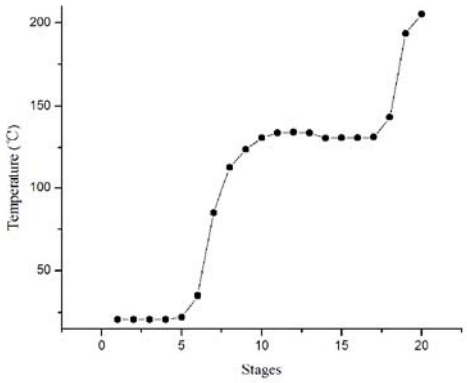

Figure 4. Temperature profiles of the catalytic reactive distillation column

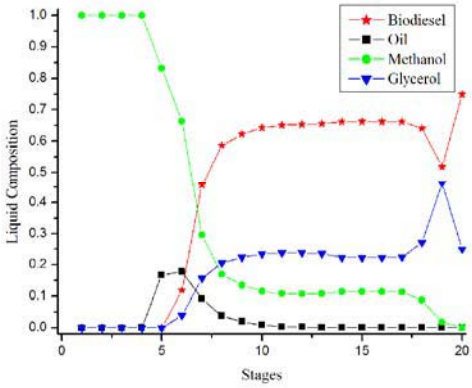

Figure 5. Liquid compositions profiles of the catalytic reactive distillation column

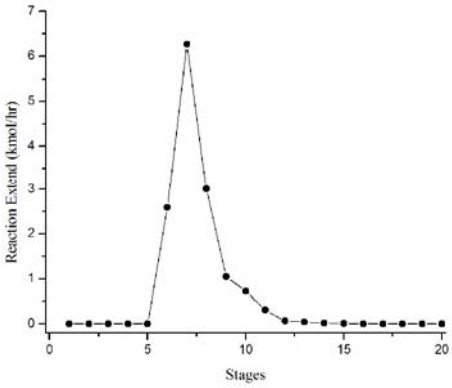

Figure 6. Reaction extend profiles of the catalytic reactive distillation column

Transesterification reaction occurred between stage 6 and stage 15. As methanol refluxed from the top was large, although methanol-to-oil ratio was only 4:1, the methanol concentration kept a high level all over the column. It conduced quick reaction rates on stages 6-10. On stage 11-15, reaction could be accomplished. Then biodiesel engendered along with glycerol flowed downward to the bottom of the column.

IV. CONCLUSION

The Antoine parameters of biodiesel and NRTL binary interaction coefficients were regressed using Aspen Plus Data Regression function according to data in literatures. Vapor pressure under different temperature and phase equilibrium condition could be simulated accurately then. Catalytic reactive distillation process for biodiesel production via transesterification was simulated using Aspen Plus successfully. Reaction and separation was integrated in one catalytic reactive distillation column. Although methanol-to-oil ratio was only 4:1, high purity (99.8% wt) of biodiesel with high yield (99.7%) was obtained. The catalytic reactive distillation process for biodiesel production via transesterification would be adequately good to have a potential industrial relevance.

ACKNOWLEDGEMENTS

The authors acknowledged the National High Technology Research and Development Program of China (2009AA03Z222), National Natural Science Foundation of China (21076044 and 20906013) and Major Scientific Research Guiding Program of Southeast University (21076044) for financial support.

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