Investigation of Optimal Esterification Conditions of Lactic Acid with Butanol by Using Response Surface Methodology

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ABSTRACT

Esterification reaction of lactic acid with butanol to produce butyl lactate and its optimal conditions were investigated. Cyclohexane was used as entrainer to remove water to promote reaction yield. Catalyst of $NaHSO_4$ was also used to increase reaction rate. Reaction parameters of butanol/lactic acid ratio, cyclohexane/lactic acid ratio, catalyst amount, and reaction time were optimized using Response Surface Methodology (RSM). Results showed that the butanol/lactic acid ratio was the most significant factor for esterification yield while interactions between butanol/lactic acid ratio and cyclohexane/lactic acid ratio, butanol/lactic acid ratio, and reaction time were less significant. The correlation coefficient between predicted values and experiment values was 0.985. The optimal conditions for the experiment are: ethanol/lactic acid ratio 5:1, cyclohexane/lactic acid ratio 1:1, catalyst loading 1.5%, and incubation period 3 hours. The esterification yield reaches 99.8% under these conditions.

INTRODUCTION

Biodiesel is usually made from renewable biological sources, such as vegetable oil and animal fats. It is biodegradable and also has lower emission profiles [1]. Nonetheless, as compared to fossil fuel, their production cost is still relatively high to be adopted as substitute fuels. Another major concern is that their huge land demand to grow sufficient plants might compete with land to grow food crops. Yet, this problem could still possibly be solved by proper utilization and management of agricultural wastes and waste oils including edible oil. Conversion of waste cooking oil into fuels can not only solve environmental problem, but also avoid its illegal reuse, repacking as edible oil returning to consumer market. One way to make biodiesel is transesterification, which is the reaction of an oil or fat with an alcohol to form esters and glycerol. However, the compositions of waste oils tend to be complicated due to a wide range of cooking methods.

Vegetable oil and animal fats are thermally decomposable. Tung oil was first thermally-cracked to yield crude oil, which was then further refined to diesel oil, gasoline, and kerosene. Catalysis has been used in many pyrolysis processes to obtain paraffin and olefins, similar to those present in petroleum sources. The main components of pyrolysis oils were alkanes and alkenes, which accounted for about 60 wt% while carboxylic acids contain 9.6 ~ 16.1% higher [2, 3]. These compositions were determined by gas chromatography–mass spectrometry (GC-MS). Chromatographic analysis showed that the pyrolyzed products still contain high portion of acid, and carbon number can be up to C18 including lower molecular weights of acetic acid and lactic acid. In this case, they are required to undergo further treatment.

In this work, we aim to use esterification to reduce the amount of carboxylic acids to increase the profit of recycling waste cooking oil. The variables adopted in esterification reaction include reaction time, temperature, alcohol/carboxylic acid ratio, water entrainer/carboxylic acid ratio, and catalyst amount. This work also uses lactic acid as a model compound to reduce acid value by reacting with butanol to produce C7 fuel. We will also develop an experimental model for esterification reaction with high yield by azeotropic distillation [4]. The water entrainer, cyclohexane, was used to remove water in the mixture by forming azeotrope with water during esterification reaction, leading to a shift from equilibrium to the product side.

METHOD

Esterification reaction is mainly affected by factors including reaction time, temperature, alcohol/carboxylic acid ratio, water entrainer/carboxylic acid ratio, and amount of catalyst as follow:

Factor	Alcohol/Acid ratio (mole/mole)	Entrainer/Acid ratio (mole/mole)	Catalyst (wt%)	Time (hour)
	A	B	C	D
-1.682	2.318:1	0.436:1	1.159	2.18
-1	3:1	0.6:1	1.5	3
0	4:1	0.8:1	2	4
1	5:1	1.0:1	2.5	5
1.682	5.682:1	1.1364:1	2.841	5.682

Because there are only four factors, we can use full factorial design to screen significant factors. We choose the 2^4 design with four central points to check the possible curvature. Table 2 shows the experimental arrangement and the corresponding yields. A second-degree polynomial model was used to express the relationship between reaction factors and yields.

$$Y = b_o + \sum_{i=1}^{4} b_i X_i + \sum_{i=1}^{4} b_{ii} {X_i}^2 + \sum_{i=1}^{4} b_{ij} X_i X_j$$

Where Y is the yield (%); b is a constant, x_1 is the ratio between alcohol and carboxylic acid; x_2 is the ratio between entrainer and carboxylic acid; x_3 is the catalyst concentration (wt%); and x_4 is the reaction time (hour). The experimental data was run by commercial software *Design Expert*, and the optimal conditions were obtained by canonical analysis, response surface plot, and contour plot through optimization analysis.

Experiment arrangement for the 2^4 design experiments

Number of run	Alcohol/Acid ratio (mole/mole)	Entrainer/Acid ratio (mole/mole)	Catalyst (wt%)	Time (hour)	Yield (%)
1	1	1	1	-1	78.27
2	1	1	-1	-1	99.80
3	1	-1	1	1	83.22
4	-1	1	-1	1	83
5	1	-1	-1	1	82.76
6	-1	-1	1	-1	82.39
7	-1	1	1	1	75.64
8	-1	-1	-1	-1	85.17
9	-1.681	0	0	0	93.92
10	1.681	0	0	0	89.34
11	0	-1.68	0	0	83.62
12	0	1.68	0	0	81.58
13	0	0	-1.68	0	97.75
14	0	0	1.68	0	87.3
15	0	0	0	-1.68	87.25
16	0	0	0	1.68	78.1
17	0	0	0	0	81.15
18	0	0	0	0	83.22
19	0	0	0	0	82.64
20	0	0	0	0	85.87

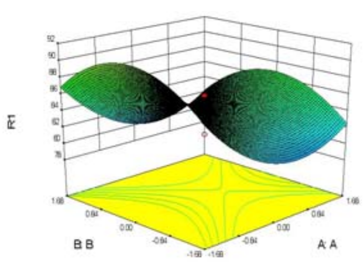
RESULTS

$$Y= 84.65728 - 1.36164\ X_1 - 0.069059\ X_2 - 3.79068\ X_3 - 2.60663\ X_4 - 3.22125\ X_2X_3 - 3.49289\ X_2X_4 + 2.07625\ X_3X_4 + 1.59776\ X_1^2 - 1.58246\ X_2^2 + 2.31193\ X_3^2 - 1.56831\ X_4^2$$

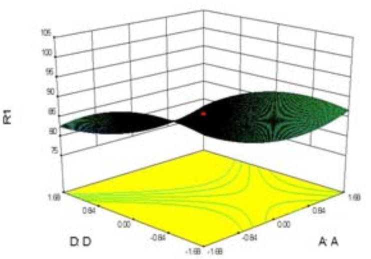
Analysis of variance of each factor (left) and each reduced factor

Source	Sum of squares	F-value	p-value
A-A	10.49	0.57	0.4846
B-B	1.94	0.11	0.7587
C-C	196.24	10.65	0.0224
D-D	41.86	2.27	0.1921
AB	0.12	0.01	0.9376
AC	12.83	0.70	0.4422
AD	2.58	0.14	0.7238
BC	83.01	4.50	0.0873
BD	40.43	2.19	0.1987
CD	34.49	1.87	0.2296
A^2	36.34	1.97	0.2192
B^2	35.65	1.93	0.2230
C^2	76.09	4.13	0.0979

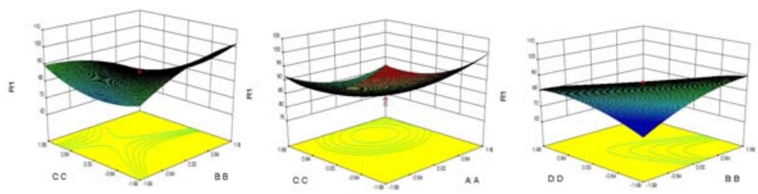
Source	Sum of squares	F-value	p-value
A-A	10.49	0.78	0.4031
B-B	0.07	0.00	0.9462
C-C	196.24	14.58	0.0051
D-D	92.79	6.89	0.0304
BC	83.01	6.17	0.0379
BD	40.43	3.00	0.1213
CD	34.49	2.56	0.1481
A^2	36.34	2.70	0.1390
B^2	35.65	2.65	0.1423
C^2	76.09	5.65	0.0447
D^2	35.02	2.60	0.1454



Effects of butanol/lactic acid ratio (A) and cyclohexane/lactic acid ratio (B) on esterification yield (R1).



Effects of butanol/lactic acid ratio (A) and reaction time (D) on esterification yield (R1)



Effects of butanol/lactic acid ratio (A), catalyst amount (C), cyclohexane/lactic acid ratio (B), and time on esterification yield (R1).

Comparison of butyl lactate yields between theoretical and experimental results

No.	Alcohol/Acid ratio (mole/mole)	Entrainer/Acid ratio (mole/mole)	Catalyst (wt%)	Time (hour)	Predicted yield (%)	Experimental yield (%)
1	-0.22	-0.36	-1.68	-1.68	97.1158	95.66
2	-0.25	-0.67	-1.68	-1.68	95.184	96.02
3	-0.39	-0.87	-1.68	-1.68	92.3381	92.03
4	1	1	-1	-1	99	99.80
5	0	0	-1.68	0	99.94	97.75

CONCLUSIONS

The esterification reaction of lactic acid with butanol was investigated in the presence of sodium bisulfate as catalyst and cyclohexane as water entrainer. Response Surface Methodology (RSM) was used to explore the relationships between independent variables as well as reaction yield. According to the results, the best conditions for the experiment are ethanol/lactic acid ratio 5:1, cyclohexane/lactic acid ratio 1:1, catalyst loading 1.5%, and incubation period 3 h, and the esterification yield is 99.8% under these conditions. From RSM analysis it was found that the butanol/lactic acid ratio was a significant factor, and the interactions between butanol/lactic acid ratio and cyclohexane/lactic acid ratio, butanol/lactic acid ratio and reaction time were less significant. The correlation coefficient of predict and experiment values was 0.985.

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