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Research on Hydrogenation of FAME to Fatty Alcohols at Supercritical Conditions

Yao Zhilong

*Beijing Institute of Petrochemical Technology, Beijing,
PRC*

1. Introduction

It is hard to develop biodiesel industry currently as a consequence of the rapid increase in the prices of animal and vegetable oil in recent years. Production of high-value bulk chemicals from biodiesel (fatty acid methyl esters) and its by-product of glycerol is an effective way to overcome the difficulties and to promote the steady development of biodiesel industry. However, the choice of target products and technologic routes for producing them should follow three principles: 1) biomass feedstocks are cheaper than petroleum products when they are used as raw materials, 2) process being developed is simple and environmentally-friendly, 3) the target products are in line with the market demands [1]. Production of fatty alcohols (FA) from fatty acid methyl esters (FAME) by hydrogenation under supercritical conditions is in line with these principles. The study on hydrogenation of FAME to FA using propane and carbon dioxide as solvents under supercritical conditions has been reported previously. But the reaction is carried out above 15.0 MPa [2-5], and such high operation pressure will seriously increase the capital and operating costs. It is thus clear that a low-pressure hydrogenation process for FAME conversion to FA under supercritical conditions can lead to reduction in the capital and operating costs of the process while the advantages of supercritical reactions are maintained, which can also lead to great social and economic benefits.

2. Experimental

2.1 Materials

The composition of the FAME of palm oil (supplied by Shijiazhuang petrochemical Co.) was shown in table 1.

A commercial copper-chromium oxide (supplied by Nanjing catalysis Factory) was used as the catalyst in this study, in the form of granule of 0.5~0.8mm average diameter, with a surface area of $73\text{m}^2\cdot\text{g}^{-1}$ and a pore volume of $0.17\text{cm}^3\cdot\text{g}^{-1}$.

Solvent A: Butane, chemical pure.

Solvent B: n-pentane, chemical pure.

Solvent C: Hexyl hydride, chemical pure.

2.2 Experimental set up

The hydrogenation reaction of FAME was carried out in 316 stainless steel downflow fixed beds, with an internal diameter of 17mm and 0.6m length, placed in oven and packed with 15g

of catalyst. The temperature of reaction was measured and controlled with thermocouples at axial positions. The production was analyzed by HP5890 gas chromatography (HP Co.), using a InoWax capillary column (HP Co.).

Contents	FAME in feedstock, Wt%
C ₁₂ FAME	0.301
C ₁₄ FAME	1.166
C ₁₆ FAME (0)	41.214
C ₁₆ FAME (1)	0.330
C ₁₈ FAME (0)	3.655
C ₁₈ FAME (1)	38.914
C ₁₈ FAME (2)	12.176
Others	2.244

Table 1. The composition of the FAME of palm oil

3. Results and discussion

3.1 Critical parameter measuring and solvent choosing

The compositions of FAME and solvent system have been measured at bubble point conditions. Peng-Roinson (PR) EOS and gas-liquid equation are used to calculate the binary interaction parameters. The critical parameter of the ternary system in which the ratio of FAME to solvent in weight is 90:10 has been predicted by PR model. The prediction reveals that the critical pressure of the ternary system is higher than 10.0 MPa as solvent A is used, and the critical temperature of the ternary system is higher than 300°C as solvent C is used. So, solvent B is chosen as the supercritical solvent in this work. It can be concluded from the study on the phase equilibrium that the critical temperature of this system increases as the ratio of FAME to solvent increases; the critical pressure of this system increases as the ratio of hydrogen to solvent increases.

3.2 Effect of the molar ratio of hydrogen to FAME

These data in figure1 were obtained under the operating conditions of the ratio of FAME to solvent B in weight is 90:10, 240°C, 9.5MPa and the reaction space velocity of 2.5-4.0h⁻¹.

These data in figure 1 show that the conversion of FAME increased with the molar ratio of hydrogen to FAME increasing when the molar ratio of hydrogen to FAME is below to 7.2 at different reaction space velocity. But, if the molar ratio of hydrogen to FAME is above 7.2, the conversion of FAME would decrease while the molar ratio of hydrogen to FAME increased. The result comparing with the conventional process of liquid-phase hydrogenolysis of fatty ester was different. The reason would be the reaction system was on supercritical conditions while the molar ratio of hydrogen to FAME was blow to 7.2 according the result of phase equilibrium. However, while the molar ratio of hydrogen to FAME was above 7.2, the reaction system was gas-liquid phase in the same way as the conditions process. So, the result shows that, to increase the reaction rate of hydrogenolysis of fatty ester, the reaction should be completed on the supercritical conditions.

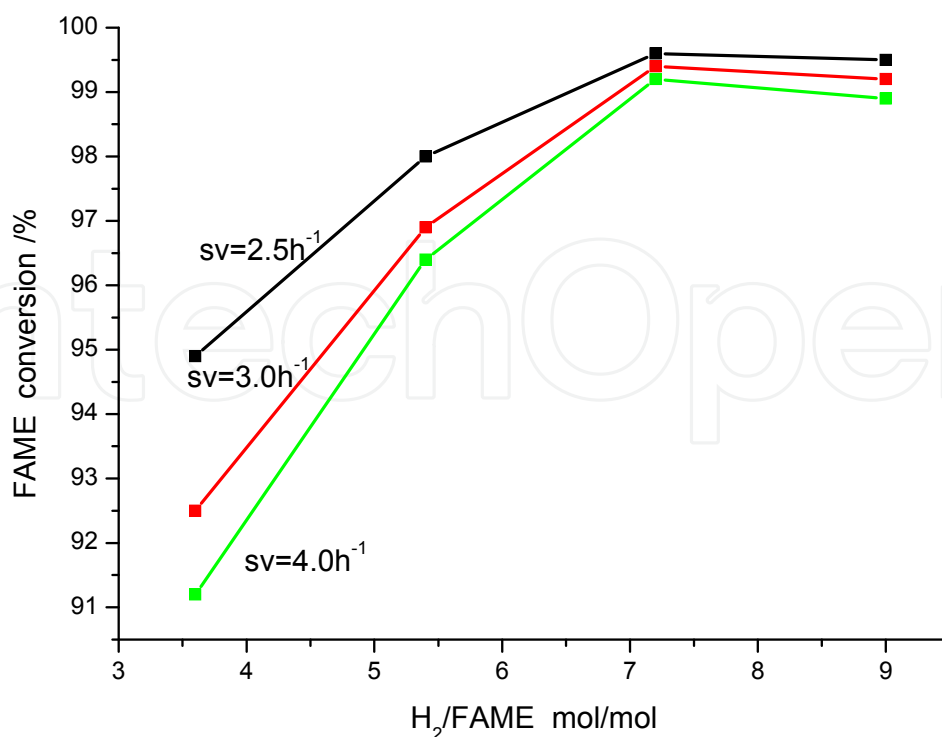


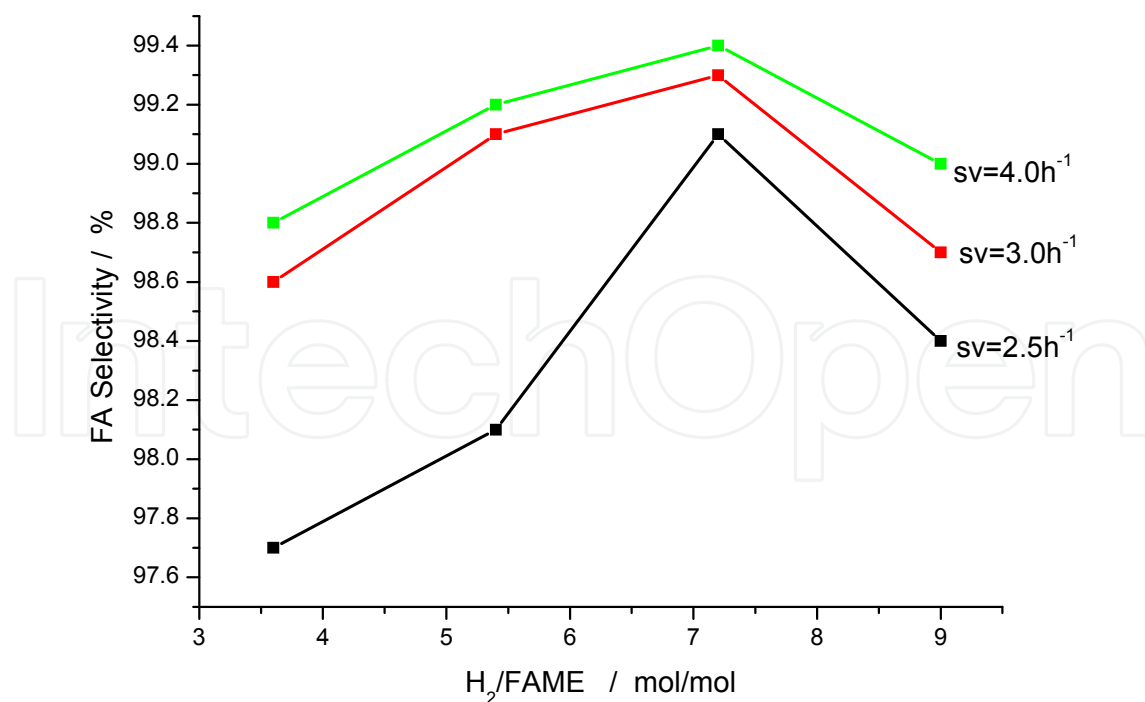
Fig. 1. The effect of the molar ratio of hydrogen to FAME

In the tradition process of hydrogenolysis of fatty acid ester, the selectivity of fatty acid ester generated lower alcohol with the reaction of hydrogen molar ratio. However, in the supercritical reaction system, the selectivity of alcohol generated with hydrogenated palm oil methyl ester increased, accompanied with molar ratio of fatty acid ester. The extreme value turned out to be around 7.2 mole ratio of hydrogen and palm oil fatty acid methyl ester, according to the date in Table 2 and Figure 2. When the mole ratio of hydrogen and palm oil fatty acid methyl ester was 7.2, the critical pressure was 9.05MPa. When the mole ratio went up to 9.0, the critical pressure went to 10.52MPa. In fact, the experimental pressure was 9.5MPa, which was in the rage of radio of hydrogen and acetate. Around 7.2 was the turning point of the change of reaction system. When the mole ratio of hydrogen and palm oil fatty acid methyl ester was less than 7.2, the reaction system was in supercritical state. Due to the polarity differences among supercritical fluids, there was a strong clustering effect between solute and solvent, solvent and solvent molecules, which made a large negative value of partial molar volume between produce and reactant near the critical point. The increase of reaction rate acted as an accumulation role to remove products promptly from the catalyst surface in order to prevent the secondary reaction with a further attempt, which means to improve the selectivity of reaction. This was also the kinetic and thermodynamic interpretation on the role of supercritical fluids to enhance the chemical reaction rate and selectivity. Among the reaction system of hydrogenated palm oil fatty acid methyl ester, the polarities between the products of alcohol and methanol were strong. However, the polarities the such reactants as palm oil fatty acid methyl ester, alkane solvents, and the reaction by products of six-alkanes and octadecane were weak. An associated effect might be caused by the products of reaction between fatty alcohol and methanol, which could remove quickly from the surface of catalyst and inhibit the further reaction of fatty alcohol to generate the side reactions of alkane. It could lead to the abnormal phenomena from the increase of the mole ratio of hydrogen and palm oil

fatty acid methyl ester, to the selectivity of palm oil fatty acid methyl ester conversion and fatty alcohol generation. When the mole ratio of hydrogen and palm oil fatty acid methyl ester was 9.0, the phase state of reaction system was deviated from supercritical state. With the decrease of associated effect, the selectivity of generated palm oil fatty acid methyl ester declined in associated with the increase of adverse reaction.

SW/h ⁻¹	H ₂ /FAME mol/mol	X _{FAME} /%	S _{FA} /%	Phase state
2.5	3.6	94.9	97.7	supercritical
	5.4	98.0	98.1	supercritical
	7.2	99.6	99.1	supercritical
	9.0	99.5	98.4	Nearly critical
3.0	3.6	92.5	98.6	supercritical
	5.4	96.9	99.1	supercritical
	7.2	99.4	99.3	supercritical
	9.0	99.2	98.7	Nearly critical
4.0	3.6	91.2	98.8	supercritical
	5.4	96.4	99.2	supercritical
	7.2	99.2	99.4	supercritical
	9.0	98.9	99.0	Nearly critical

Table 2. The effect of the molar ratio of hydrogen to palm oil FAME to the selectivity of fatty acid ester



Reaction Temperature: 240°C; Reaction pressure: 9.5MPa

Fig. 2. The effect of the molar ratio of hydrogen to palm oil FAME to the selectivity of fatty acid ester

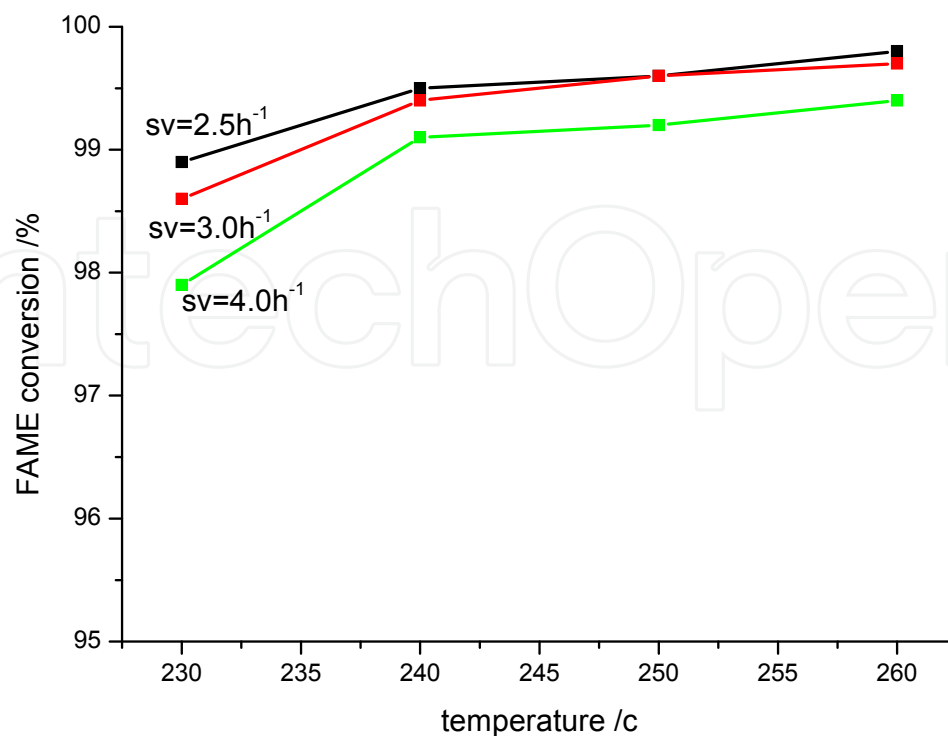
3.3 The impact of reaction temperature

As what has been discussed above, the thermodynamic analysis that fatty alcohol was generated by hydrogenolysis of fatty acid methyl esters has shown that the equilibrium constant of this reaction decreased by the increase of reaction temperature. The side reaction of fatty alcohol with further hydrogenation was an endothermic reaction. The equilibrium constant increased with increasing temperature. As a matter of fact, from the point of thermodynamic view, the reaction should be done in a lower temperature in order to obtain higher product selectivity purpose. From the reaction kinetics point of view, the reaction rate increased as reaction temperature raised. Therefore, it was necessary to compromise between reaction rate and purpose product selectivity, and to select appropriate conditions of supercritical hydrogenation process on fatty acid methyl ester. According to catalyst pretreatment and catalytic properties results and the results of reaction system equilibrium, in the condition of the test materials which the mass ratio of fatty acid methyl ester and solvent was 10:90, the response pressure was 9.5MPa, the molar ratio of hydrogen to fatty acid methyl ester of 7.2, the results have been shown on Table 3, Figure 3 and Figure 4 in the range of 230~270°C.

Table 3, Figure 3 and Figure 4 shown the conversion rate of fatty acid methyl ester increased slightly with the raise of reaction temperature in the supercritical state. Although from the thermodynamic perspective, the reaction equilibrium constant of hydrogenolysis of fatty acid methyl esters decreased with temperature rising, from reaction kinetics perspective, the reaction rate was accelerated with increasing reaction temperature. Due to that fact, when reaction deviated from chemical equilibrium, the overall performed that the conversion rate of fatty acid methyl esters increased with the reaction temperature rising. The side reaction of hydrogenated alkane is an endothermic reaction. The purpose product selectivity was unfavorable whether from the perspective of thermodynamics or kinetics. The experiential results also showed that the purpose product selectivity of fatty acid methyl ester decreased significantly as the reaction temperature raised.

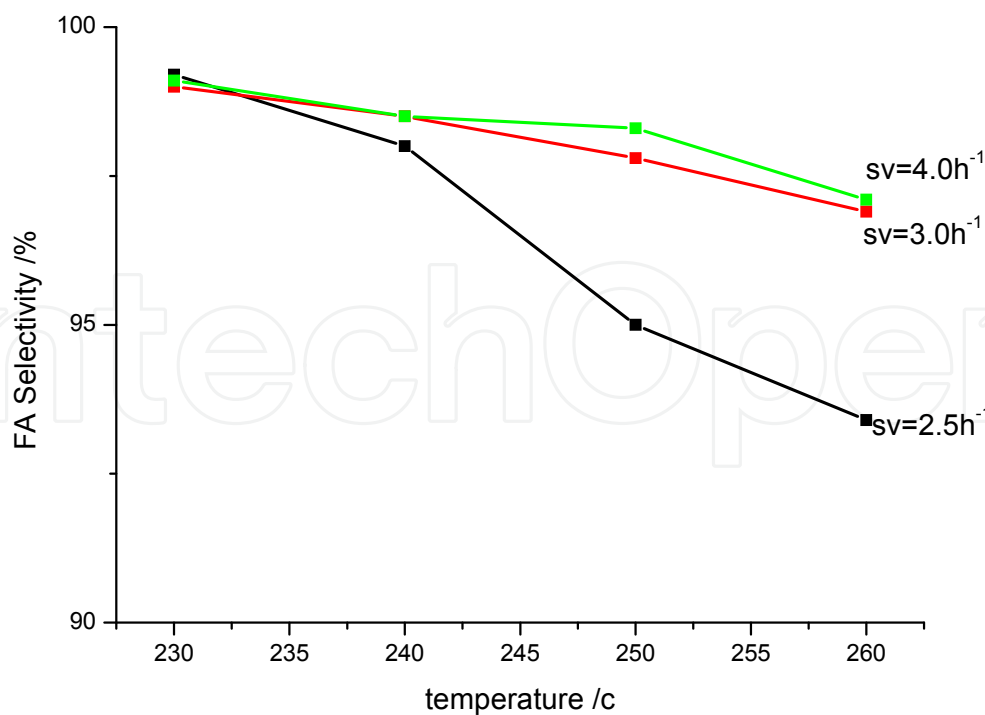
SW/h ⁻¹	Temperature /°C	X _{FAME} /%	S _{F_A} /%	Phase state
2.5	230	98.9	99.4	supercritical
	240	99.5	99.1	supercritical
	260	99.8	94.4	supercritical
3.0	230	98.6	99.5	supercritical
	240	99.4	99.3	supercritical
	250	99.6	98.8	supercritical
	260	99.7	96.9	supercritical
4.0	230	97.9	99.6	supercritical
	240	99.1	99.4	supercritical
	250	99.2	98.3	supercritical
	260	99.4	97.1	supercritical

Table 3. The Impact of Reaction Temperature (Reaction pressure 9.5MPa, the molar ratio of hydrogen to FAME 7.2)



Reaction conditions: Reaction pressure: 9.5Mpa, the molar ratio of hydrogen to FAME:7.2

Fig. 3. The effect of the Reaction temperature to the conversion of the palm oil FAME



Reaction conditions: Reaction pressure: 9.5Mpa, the molar ratio of hydrogen to FAME:7.2

Fig. 4. The effect of the Reaction temperature to the selectivity

3.4 The impact of space velocity

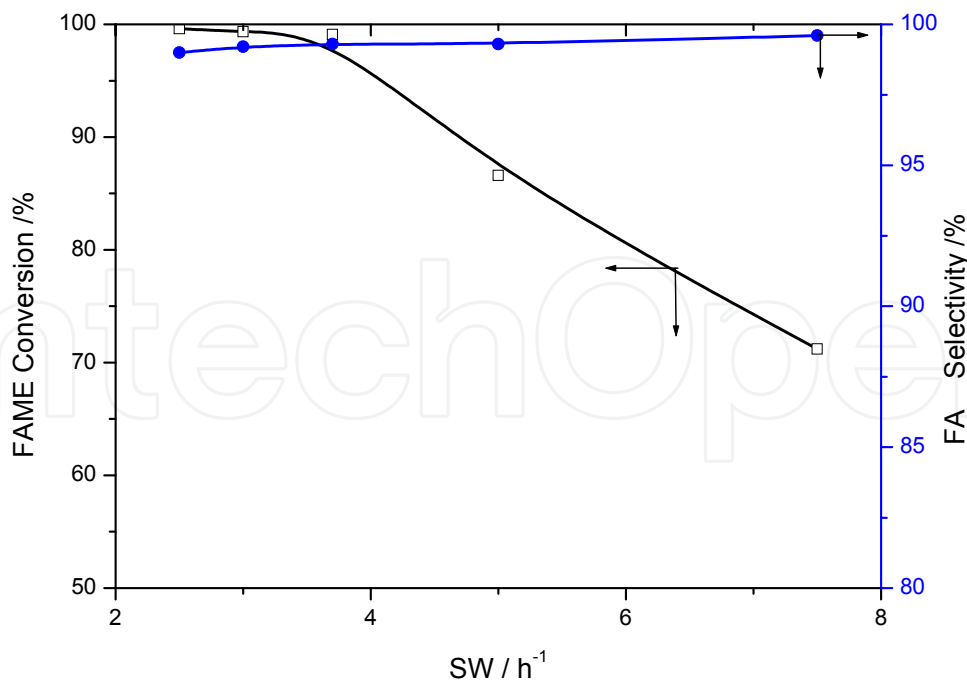
In the process of heterogeneous catalysis, the space velocity of reactant, which is one of the important parameters in the process of heterogeneous, reflected the reaction materials and the catalyst contact time directly. The experimental results which contained reaction materials made of palm oil fatty acid methyl ester and solvent in the ratio of 10:90 have shown in Table 4 and Figure 5 in the condition of reaction temperature 240 °C, molar ratio of hydrogen esters 7.2, reaction pressure 9.5MPa, in order to research how the space velocity (including mixed material with solvent contained) affected the reaction results.

According to the data from Table 4 and Figure 5, the conversion rate of fatty acid methyl ester increased with the space velocity decreased. However, the selectivity of product fatty alcohol generated by fatty acid methyl ester increased slightly with the space velocity increased. This was due to the increasing space velocity, short time contacted by reaction mixture and catalyst.

Reaction Space Velocity /h-1	2.5	3.0	3.7	5.0	7.5
Methyl ester conversion / %	99.6	99.35	99.1	86.6	71.2
The selectivity of alcohol / %	99.0	99.2	99.3	99.3	99.6
System state	Supercritical	Supercritical	Supercritical	Supercritical	Supercritical

Reaction conditions: Reaction temperature 240°C, the molar ratio of hydrogen to FAME 7.2, Reaction pressure 9.5MPa

Table 4. The Impact of Space Velocity



Reaction conditions: Reaction temperature 240°C, the molar ratio of hydrogen to FAME 7.2, Reaction pressure 9.5MPa

Fig. 5. The effect of Space Velocity to the conversion and selectivity

This also indicated that reaction was controlled by kinetics in the condition of the space velocity. Besides, the data in Table 4 and Figure 5 shows that the conversion rate of fatty acid methyl ester was above 99% with the condition of less than 4.0h^{-1} space velocity. While in terms of purpose products, it was more than 90%, and increased slightly with space velocity increased. Compared with $0.15\sim 0.4\text{h}^{-1}$ space velocity which calculated according to tradition process of hydrogenolysis of fatty acid methyl ester, supercritical reaction technology was taken, but there was 90% solvent remaining in reaction materials. When the space velocity of mixture made of solvent and fatty acid methyl ester was 4.0h^{-1} , the space velocity of fatty acid methyl ester was around 0.4h^{-1} . There was no significant difference between them. That means compared with tradition technology, taking new supercritical reaction technology to deal with the same amount of fatty acid methyl ester did not change the size of reactor by increasing supercritical solvent. In other words, it was able to enhance the production strength of fatty alcohol.

3.5 The impact of operating pressure

According to the situation of hydrogenation of fatty acid methyl ester, when the composition of fatty acid methyl ester, solvent and hydrogen was constant, the reaction system could change into different phase state by transforming the system operating pressure in a certain degree. Therefore, operating pressure could not only affect the reaction result, but also affect the system operating pressure. The experimental materials on the pressure effect research is the mixture solution with mass ratio of 10:90 on fatty acid methyl ester and solvent. Experimental results by different operating pressures are shown in Table 5 and Figure 6 on the condition of reaction temperature 240°C , the molar ratio of hydrogen fatty acid methyl ester 7.2, and the space velocity of mixed solution weight 4.0h^{-1} .

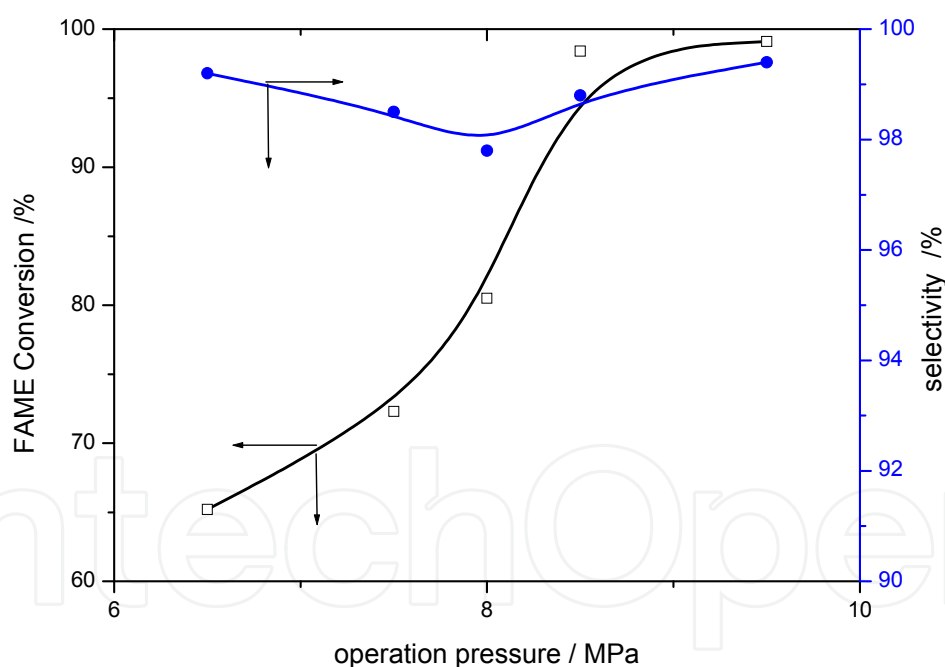
According to Table 5 and Figure 6, as the pressure increased, the conversion rate of fatty acid methyl ester increased. When the pressure rose to 8.0MPa , the conversion rate increased rapidly. The purposed product selectivity of fatty alcohol rose with the reaction pressure. The minimum was occurred with around 8.0MPa of the operating pressure. The research results on the reaction equilibrium shows that the critical pressure of reaction system was 9.0MPa due to the composition of experimental materials. It means that when the operating pressure reached 8.0MPa , the phase reaction was close to the critical state. When the operating pressure was up to 9.5MPa , the reaction system was in the supercritical state. That also shows that when the operating pressure was lower than 8.0MPa , the hydrogen solubility increased in the reaction medium as the increasing operating pressure. It reduced the mass transfer resistance, and led to the fatty alcohol generated by hydrogenation of fatty acid methyl ester and the reaction rate with hydrogen added to generate alkanes increased. The conversion rate of fatty acid methyl ester increased as the pressure increased, and the purposed product selectivity decreased as the pressure increased. The reaction system was up to the supercritical state in the same situation. The reaction system was changed from gas-liquid phase to supercritical fluid phase. The mass transfer resistance of hydrogen in the reaction medium was eliminated. The conversion rate of fatty acid methyl ester increased significantly, when the operating pressure was over 8.5MPa . Due to the fact that when the reaction pressure was close or up to the reaction system critical point, the product of fatty alcohol, the association of the product of fatty alcohol and methanol improved gradually. The speed of removing from fatty alcohol to catalyst surface in time was increased. It could benefit the local composition which was good to purpose response. It also reduced the further alkane generation of adverse reaction

from fatty alcohol. Therefore when the reaction pressure was close or up to the reaction system critical point, the purposed product selectivity of fatty alcohol rose with the reaction pressure. That led to the minimum of selectivity of fatty alcohol was occurred by the change of the operating pressure. The results of phase equilibrium and calculated reaction system stimulation which were reasonable were proved by the regularity that the operating pressure affected the reaction results.

Reaction pressure /MPa	6.5	7.5	8.0	8.5	9.5
Methyl ester conversion / %	65.2	72.3	80.5	98.4	99.1
The selectivity of fatty alcohols / %	99.2	98.5	97.8	98.8	99.4
System state	Gas - liquid	Gas - liquid	Subcritical	Nearly critical	supercritical

Reaction conditions: Reaction temperature 240°C, the molar ratio of hydrogen to FAME7.2, Weight Space Velocity of the mixed solution 4.0h⁻¹

Table 5. The Impact of Operating Pressure



Reaction conditions: Reaction temperature 240°C, the molar ratio of hydrogen to FAME 7.2, Weight Space Velocity of the mixed solution 4.0h⁻¹

Fig. 6. The Impact of Operating Pressure

3.6 Analysis of reaction products

The fatty alcohols produced from this process have been evaluated, as shown in table 6. Comparing the data in table 6 and table 7, the results show that the properties of these products meet the GB/T 16451-1996 specifications.

Compose	Content /%
FAME	0.73
FA	98.77
Alkane	0.50

Table 6. The compose of reaction products

Type		Appearance	MP/°C	Content of alkane/ %	Content of FA/ %
C _{16~18} FA	Superior quality	White flaky	48-58	≤0.5	≥95
	First quality			≤1.0	≥90
	Qualified			≤2.0	≥85

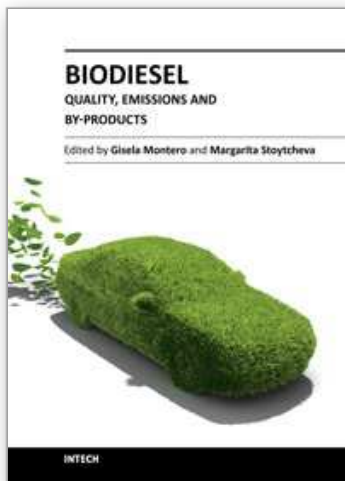
Table 7. GB/T 16451-1996 specifications of nature fatty alcohols

4. Conclusion

For FAME of palm oil, the proper supercritical conditions are as follows: molar ratio of hydrogen to FAME of 5.4-7.2, 240-250°C, 9.0-9.5MPa, and the reaction space velocity of 2.5-4.0h⁻¹, respectively. It has been shown that conversion of more than 99% and about 99% yield of fatty alcohol can be achieved at the optimized reaction conditions. A comparison between the novel hydrogenation technology under supercritical conditions in this work and the conventional process of liquid-phase hydrogenolysis of fatty ester shows that the ratio of hydrogen to FAME in reaction system is reduced by 90-98%, and the temperature and pressure of reaction is decreased significantly also in this work. It can be concluded from the reaction conditions that the pressure of this novel process here is lower by about 5.0 MPa than that for the process reported by other researcher^[4].

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This book entitled "Biodiesel: Quality, Emissions and By-products" covers topics related to biodiesel quality, performance of combustion engines that use biodiesel and the emissions they generate. New routes to determinate biodiesel properties are proposed and the process how the raw material source, impurities and production practices can affect the quality of the biodiesel is analyzed. In relation to the utilization of biofuel, the performance of combustion engines fuelled by biodiesel and biodiesels blends are evaluated. The applications of glycerol, a byproduct of the biodiesel production process as a feedstock for biotechnological processes, and a key compound of the biorefinery of the future is also emphasized.

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Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
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www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

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