

Hydrogenation of fatty acid methyl ester to fatty alcohol at supercritical conditions

HUANG Hui, FAN Chunling, CAO Guiping*

State Key Lab of Chemical Engineering, East China University of Science & Technology,
Shanghai, 200237, P R China. gpcao@ecust.edu.cn +86-21-64253528

ABSTRACT

Hydrogenation of various types of oleochemicals is a major unit operation in industry. Natural fatty alcohols are important raw materials for surfactants and lubricants and can be produced by catalytic hydrogenation of fatty acid methyl esters (FAME). Commercial multiphase processes are necessarily operated at high pressures and high hydrogen-to-ester mole ratio owing to low solubility of hydrogen in liquid phase. Using the supercritical fluid, a substantially homogeneous supercritical phase could be created, whereby hydrogen could completely access to the active site of the solid catalyst. In this paper, the supercritical hydrogenation was studied in a batch, stirred reactor. The results showed that adding of the propane prompt the mass transfer of hydrogen to the catalyst and increase the concentration of hydrogen on the catalyst surface. It was found that the reaction time and the hydrogen-to-ester mole ratio were two key factors affecting the conversion. The conversion increased from 14% to 96% as the reaction time prolonged from 15min to 240min at the hydrogen-to-ester mole ratio of 11, and the conversion increased from 54% to 97% as the hydrogen-to-ester mole ratio increased from 8.8 to 21.6 at the reaction time of 150min. Compared with traditional batch hydrogenation, the concentration of reactants on the catalyst surface could be controlled effectively in supercritical condition, which could promote the selectivity of lauryl alcohol from 80% to 95% above and reduce the hydrogen-to-ester mole ratio from about 100 to 20 below.

INTRODUCTION

Natural fatty-alcohols derived from renewable resources, such as plant oils and animal oils, have become the important base feedstock for the production of cationic, anionic and nonionic surfactants [1,2]. These fatty-alcohol-based surfactants have also gained more growing significance in the detergent market in the past few years, due to their excellent washing properties and superior biodegradability compared to conventional detergents made from petrochemicals [3].

The industrial route from natural fats and oils to fatty alcohols generally proceeds via hydrolysis of triglycerides to fatty acids, esterification to methyl esters and hydrogenation of methyl esters to fatty alcohols [4]. The last step is usually a catalytic process carried out in slurry or fixed-bed reactor using a copper-based catalyst with the following typical conditions: hydrogen pressures between 20 and 30MPa, and temperatures ranging from 200 to 300°C [5,6]. Such rigorous conditions are required in view of the poor solubility of hydrogen and the high mass-transfer resistance in the methyl ester, which leads to a shortage of hydrogen at the

catalyst surface. Moreover, high operating pressures and a very large excess of hydrogen, seriously brought a large equipment investment, high operating costs and low security. This above explains the efforts made to arrive at low-pressure processes and low hydrogen-to-ester molar feed ratios.

The favorable solvent and transport properties of supercritical fluids make them an adequate medium for chemical reactions and offer great opportunities for process improvement. Härröd, Andersson, Brands and their co-workers have provided convincing evidence that hydrogenation of fats/oils and oleochemicals were feasible under supercritical conditions, using agents as supercritical CO₂, supercritical propane or supercritical butane [7-15].

Traditional methods utilize batch, stirred reactor operation resulting in long reaction times and excessive use of catalyst and hydrogen. To gain further insight in the influence of propane and hydrogen-to-ester molar ratio on the process, batch hydrogenation of dodecyl methyl ester to dodecanol at supercritical conditions was taken as a model reaction using co-precipitation prepared copper zinc catalyst.

MATERIALS AND METHODS

The copper zinc catalyst was prepared by parallel co-precipitation method. The catalyst was reduced under 10 ml/min of hydrogen by heating to 240°C at a rate of 5 °C/h and then cooled to room temperature under the atmosphere of hydrogen. The obtained catalyst was then transferred in nitrogen atmosphere and stored in dodecyl methyl ester before used.

The basic experimental apparatus for studying the hydrogenation of methyl ester under supercritical conditions was operated in a visual system and a batch experimental system. The visual system was used to observe the status of reactant mixtures under given temperature and pressure, and hydrogenation reactions were performed in the batch experimental system. products were analyzed by a GC equipped with a flame ionization detector (FID). 1-octanol was used as the internal standard compound for analysis. All components were identified by Micromass GCTTM GC-mass spectroscopy.

RESULTS

In the traditional process of fatty acid methyl ester hydrogenation, the influence of temperature on the reaction mainly reflected by the variation of catalytic activity. The choice of the reaction temperature depended on the activation temperature of the catalyst and the by-product. The positive effect of increment of temperature on reaction rate became slighter in the case that the temperature exceeds the activation temperature of the catalyst [16]. However, high temperature is in favor of generation of the alkane. In the supercritical process, the temperature affects the phase equilibrium of hydrogen and fatty acid methyl ester in supercritical propane, besides above two effects. The increment of temperature would decrease the homogeneous phase region, as well as the feasible operating region for supercritical hydrogenation [5,9]. In this study, the reaction temperature was fixed at 240°C.

The homogeneous phase region could broaden as pressure increases. The reaction pressure maintains between 15 and 18MPa for feasible supercritical operating region. Phase equilibrium experiments were performed in the visual system and the results were given in Tab. 1.

Tab.1 Phase equilibrium experiments

C_{FAME} mol%	C_{hydrogen} mol%	C_{propane} mol%	status
0.5	16.2	83.3	homogeneous
1.0	22.3	76.7	homogeneous
2.5	51.8	45.7	heterogeneous

$T=240^{\circ}\text{C}, P=15.2\text{MPa}$

The propane was used to balance the system pressure as the variation of pressure in the reaction could affect the reaction results. The effect of propane amount on reaction results was tested as shown in Tab. 2. Based on GC-EOS phase equilibrium computation, the status of the reaction system under conditions that the value of propane/FAME mole ratio is 20.88, 43.15 and above 80, is non-, sub- and supercritical respectively. As shown in Tab.2, the amount of propane has no effect on the reaction results under supercritical conditions.

Tab.2 Reaction results of different $\text{C}_3\text{H}_8/\text{FAME}$ mole ratio

$n_{\text{propane}}:n_{\text{FAME}}$ mol/mol	x %	s_{FOH} %
20.88	98.12	79.94
43.15	97.15	93.20
81.70	93.54	95.93
88.20	92.76	96.40
97.40	92.96	96.34

$T=240^{\circ}\text{C}, t=150\text{min}$

Fig. 1 shows the relationship between agitation speeds and reaction results under non- and supercritical conditions. Compared with the traditional hydrogenation process, the minimum agitation speed, which should be met for eliminating external diffusion, is much lower in supercritical process, 400rpm, other than 600rpm, is feasible. The introduction of propane increased the solubility of hydrogen in reactant and enabled the above variation of agitation speed happen. Supercritical process also relieved the enrichment of dodecanol at the catalyst surface and reduced the intermediate product dodecyl dodecanoate.

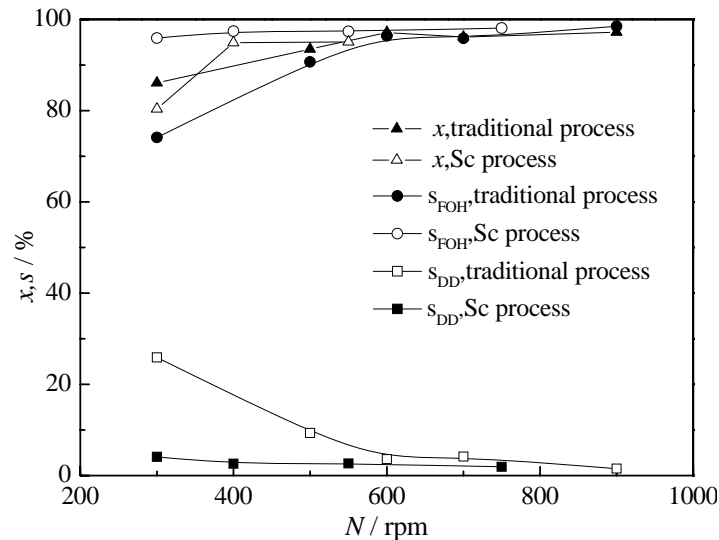


Fig.1 Relationship of reaction results and agitation speeds
 S_{FOH} : selectivity of dodecanol; S_{DD} : selectivity of dodecyl dodecanoate
 Sc hydrogenation: $c_{\text{FAME}} = 1.0\text{mol}\%$, $n_{\text{H}_2}:n_{\text{FAME}} = 16.6$, $P = 15.6\text{MPa}$
 Traditional hydrogenation: $P = 22\text{Mpa}$, $T = 240^\circ\text{C}$

Fig.2 shows that the conversion of methyl laurate grows from 13.95% to 96.32% with the reaction time increases from 15min to 240min. The reaction time has no effect on the selectivity of lauryl alcohol and dodecyl dodecanoate in supercritical process.

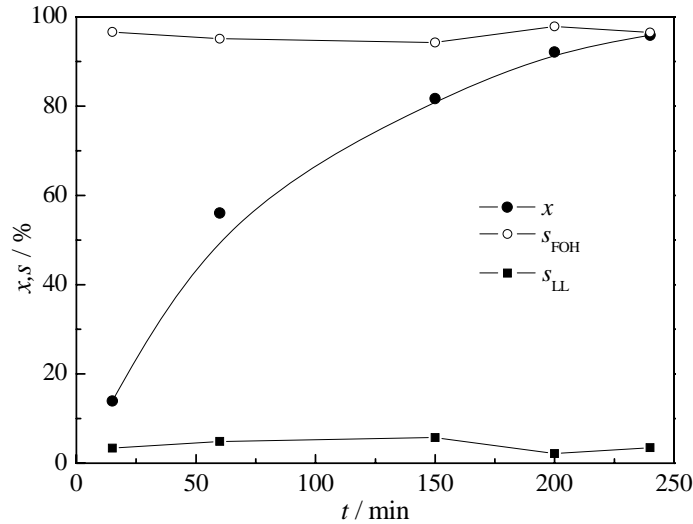


Fig.2 Relationship of reaction results and reaction time
 Sc hydrogenation: $c_{\text{FAME}} = 1.0\text{mol}\%$, $n_{\text{H}_2}:n_{\text{FAME}} = 11$, $P = 15.2\text{MPa}$

Hydrogen-to-ester ratio is an important process parameter in hydrogenation reaction. Commercially, high hydrogen-to-ester mole ratio ranging from 50 to 100 is required for an appropriate solubility of hydrogen in ester. As shown in Fig. 3, the conversion increases with the hydrogen-to-ester mole ratio getting higher at a fixed reaction time. When reaction time is 150min, the conversion increases from 53.84% to 96.75% as hydrogen-to-ester mole ratio increasing from 8.8 to 16.6, and the conversion nearly have no increment as hydrogen-to-ester mole ratio increasing from 16.6 to 21.6. In other words, the reaction is close to completion at the hydrogen-to-ester mole ratio of approximately 17. When reaction time is 40min, the conversion increases from 50.26% to 89.67% while hydrogen-to-ester mole ratio i increasing from 11.6 to 20.6. It indicated that higher hydrogen-to-ester mole ratio has positive effect on the increment of the conversion. However, according to phase equilibrium, the homogeneous phase region restricts the system composition of the reaction mixtures, the operating point would exceed the homogeneous phase region as the value of hydrogen-to-ester mole ratio is too large.

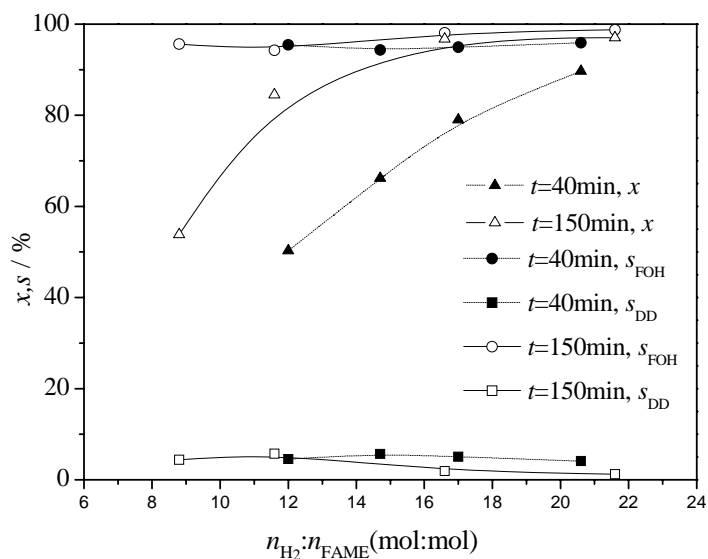


Fig.3 Relationship of reaction results and H₂/FAME mole ratio at different reaction time ($c_{\text{FAME}}=1\text{ mol}\%$)

From Fig.4, It could be concluded that conversion increases with the hydrogen-to-ester mole ratio at the same concentration of methyl ester. While at the same hydrogen-to-ester mole ratio, the conversion is higher at a higher concentration of methyl ester. This may be caused by the fact that the existence of excess supercritical propane and hydrogen made the methyl ester to become a controlling factor of the reaction and a higher concentration of methyl ester means a faster reaction rate. As shown in Fig.4 and other figures above, it can be found that the selectivity of aluryl alcohol in supercritical conditions were all above 95%, and the homogeneous phase reduced the mass transfer resistance which enable concentration of reactants on the catalyst surface to be controlled effectively.

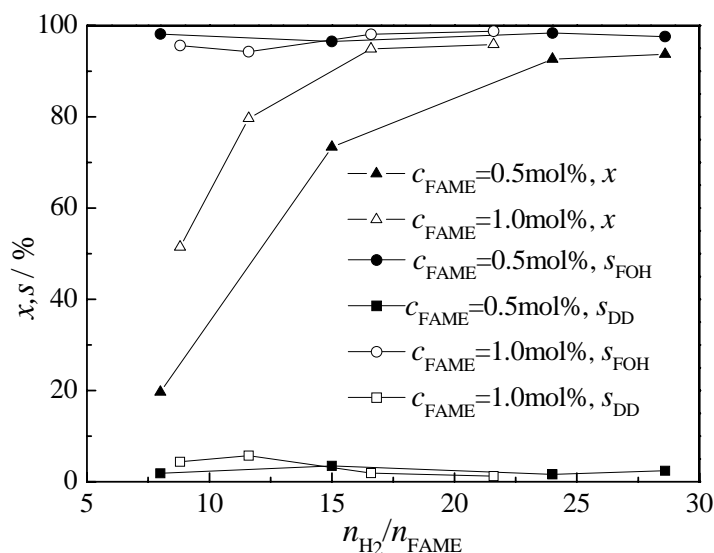


Fig.4 Relationship of reaction results and H₂/FAME mole ratio ($t=150\text{min}$)

CONCLUSION

(1) Suitable reaction temperature, pressure, hydrogen-to-ester mole ration and the amount

of propane were discussed for obtaining a homogeneous reaction phase. The amount of propane would have no effect on the hydrogenation reaction results when the reactions were carried out in the homogeneous phase.

(2) The reaction time and the hydrogen-to-methyl ester mole ratio were two key factors affecting the conversion of the reaction in supercritical conditions. The conversion increases with the increment of the reaction time and the hydrogen-to-methyl ester mole ratio and it could reach as high as about 97% at the following given reaction conditions: concentration of methyl ester is 1mol%, hydrogen-to-methyl ester mole ratio is about 16 and reaction time is 150min.

(3) Compared with traditional batch hydrogenation, the concentration of reactants on the catalyst surface could be controlled effectively in supercritical condition, which could promote the selectivity of lauryl alcohol, inhibit the generation of alkane and reduce the hydrogen-to-methyl ester mole ratio.

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