SUPERGEN Bioenergy Hub

Bioenergy Hub Small Grant Report

Title of Project
Feasibility study of ultrasound-enhanced catalytic esterification of pyrolysis bio-oil
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Organisation: University of Hull
Period of Project: 01/09/2015-31/08/2016

Objectives of work
The project aims to investigate the combined effects of catalysis and ultrasound on the upgrading of bio-oil, with the following objectives:

- Design and build a laboratory scale ultrasound catalysis reaction system
- Catalyst development and test
- Experimental studies of the effects of the key parameters including reaction temperature, catalyst to sample ratio and the power of ultrasound on the reaction rates

1. Development of fixed-bed reactor and carry out esterification reactions

In this work, an ultrasonic probe was initially obtained to investigate the enhancement of ultrasound on the catalytic esterification of acetic acid. At first, acetic acid was used as a model compound for real bio-oil, as the removal of organic acid from pyrolysis bio-oil is one of the key objectives for the upgrading of pyrolysis bio-oil.

Figure 1 Experimental Setup for Esterification

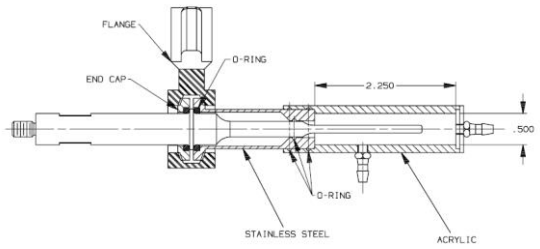


Figure 2 Diagram of a mini flow ultrasonic reactor

2. Development of a continuously reactor

During the development of the reaction system, a mini flow reactor cell (shown in Figure 2 and 3) was selected for continuous reaction.
Figure 4 shows the continuously ultrasonic catalysis esterification reaction system. The reactor is heated by a water batch. Inside the reactor, liquid (reactants) is

circulated using a pump. Liquid samples can be collected at different reaction time, and be analysed by titration or FTIR.

Figure 3 Pictures of the mini flow reactor

Figure 4 Continuously reaction system

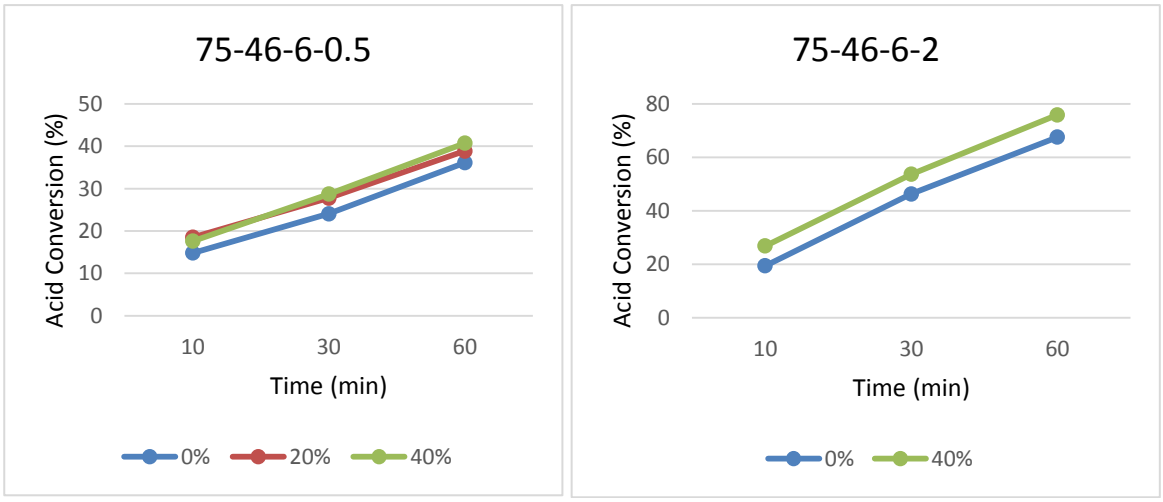
3. Catalyst development

In this work, WO_3/ZrO_2 catalysts were prepared and tested for the esterification of acetic acid under the combination of ultrasound and catalysis. A wetness impregnation method was used. During the catalyst preparation, aqueous solutions of ammonium tungstate hydrate was mixed with certain amount of WO_3 support. The mixture of catalyst precursor was stirred for around 10 h, and then dried at 100 °C overnight. Finally, the catalysts were calcined at 750 °C for 3 h with a heating rate of 1 °C/min.

5 wt.% W/ZrO_2 catalyst was improved in terms of the acid sites by refluxing with a 15% H_2SO_4 solution at 60 °C for 1h.

4. Results and discussion

4.1 Using commercial Amberlyst-15 catalyst with the fixed-bed reactor

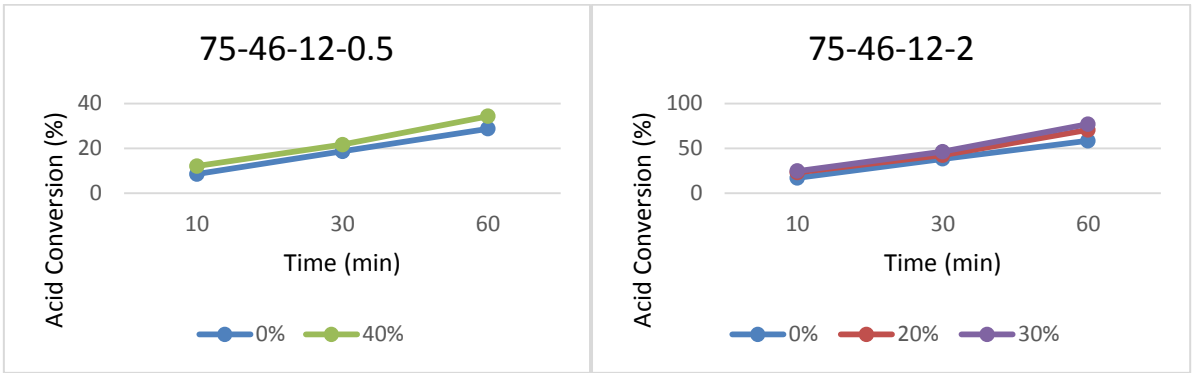


(a) (b)

Figure 5. The effects of ultrasound power on acetic acid conversion at 75 °C, ethanol 75 g, acetic acid 6 g; (a) 0.5 g catalyst; (b) 2 g catalyst

Error! Reference source not found. (a) and (b) show the influence of ultrasound power on the acetic acid conversion at75°C, ethanol of 46 g, acetic acid of 6 g, and catalyst of 0.5 and 2 g,

respectively. Based on the figures above, it can be seen that there is an improvement of acetic acid conversion in correlation with the ultrasound power (~10%). In addition, the plots show a near linear relationship throughout the results.



(a) (b)

Figure 6 Influence of ultrasound power on acetic acid conversion at 75 °C, ethanol 75 g, acetic acid 12 g; (a) 0.5 g catalyst; (b) 2 g catalyst

Figure 6 (a) and (b) show the influence of ultrasound power on the acetic acid conversion at 75°C, ethanol of 46 g, acetic acid of 12 g, and catalyst of 0.5 and 2 g, respectively. From Figure 6 (a), the results show that ultrasound power influences the acetic acid conversion and also have a near linear relationship. The conversion of acetic acid was increased 28 to 34% when 40% of ultrasound power was used. However, there is a slight decrease in the acid conversion with the use of 12 g of acetic acid as compared to the previous results which uses 6 g of acetic acid.
When more catalyst was used (2 g), as shown in Figure 6 (b), the enhancement of ultrasound was bigger, for example, at 60 mins, the conversion of acetic acid was increased by 18% when 30% of ultrasound power was used.

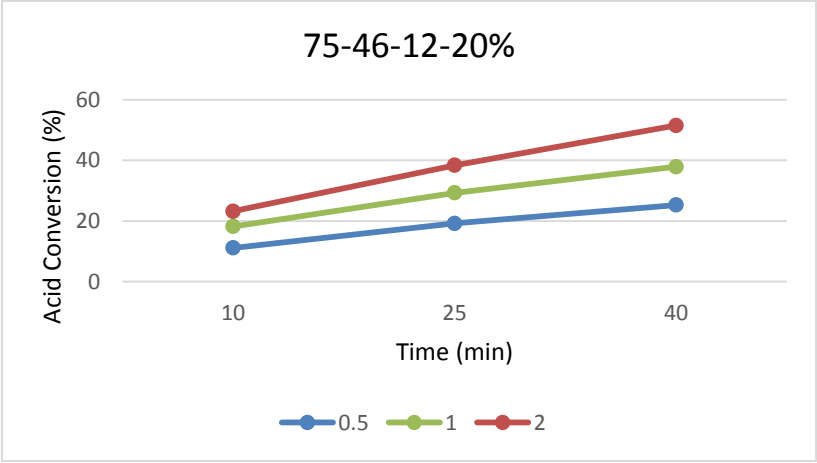


Figure 7 Influence of catalyst amount on acetic acid conversion at 75 °C, ethanol 75 g, acetic acid 12 g, and ultrasound power 20%

Error! Reference source not found. shows the influence of catalyst amount on the acetic acid conversion at75°C, ethanol of 46 g, acetic acid of 12 g, and ultrasound power of 20 %. It can clearly be seen that the amount of catalyst indeed has an effect on the acetic acid conversion during the esterification process. The plot also shows a near linear relationship which is consistent with the aforementioned results. On the other hand, the time intervals between each collection of sample

for this experiment were shorten to 10, 25, and 40 minutes as it was concluded that there is no significant difference in the results with a longer time scale.

4.2. Using WO_3/ZrO_2 catalysts

The fresh WO_3/ZrO_2 catalyst after calcination at 750 °C showed little effect of the conversion of acetic acid. It is suggested that the number of acid sites were not enough for the reactions under the current investigated conditions (low temperature and atmosphere pressure).

However, we have tried the sulfuration of the catalyst (20% WO_3/ZrO_2) to increase the acidity of the catalyst. The results were shown in Figure 8. After the sulfuration, about 30% of acid conversion was obtained at 30 mins reaction time. However, it looks like the conversion rate was increased only from 24.2 to 28.2% when the reaction time increased from 20 min to 30 min, compared to an increase from 12.1 to 24.2% when the reaction time was increased from 10 mi to 20 min. It is suggested the acid site was lost during the reaction. Therefore, the catalyst after sulfuration was calcined at around 500 °C with the purpose to stabilize the acid sites. However, as shown in Figure 8, after the calcination of the catalyst, the conversion of acid was significantly reduced, although a linear relationship between the reaction time and the conversion was obtained. Thus, it is suggested that the presence of acid site is key for the conversion of acetic acid in this work.

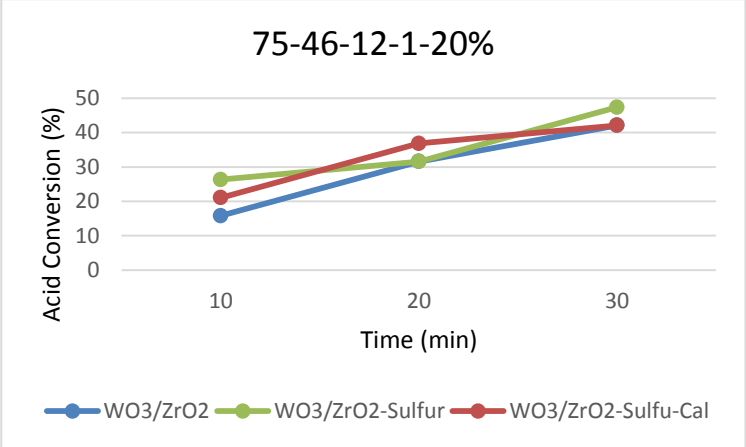


Figure 8 Conversion acetic acid at temperature of 75 °C, ethanol 75 g, acetic acid 12 g, and ultrasound power 20%, and with different catalysts

4.3. Using real bio-oil produced from biomass pyrolysis

In this work, real bio-oil obtained from pyrolysis of biomass was used for the investigation of the combined catalysis and ultrasonic esterification. The bio-oil was diluted with ethanol prior to the experiment, in order to ensure the homogeneity of the bio-oil. The commercial Amberlyst catalyst was used.

As shown in Figure 9, although the conversion of acid was increased with the increase of reaction time, the influence of the power of ultrasound is difficult to be obtained.

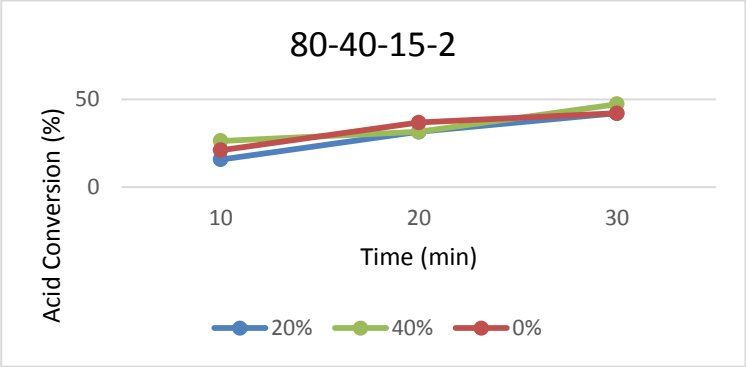


Figure 9 Influence of ultrasound power on acetic acid conversion at temperature of 80 °C, ethanol 40 g, bio-oil 15 g, 2. g catalyst

5. Application of using synchrotron B22 beam line for future work

Currently, the analytical method (titration using NaOH solution) we used can only measure the conversion rate acetic acid, while the time-resolved composition of the liquids was unknown. Hence, the influence of ultrasound processing cannot be assessed fully because the ultrasound effect is concentrating within the region where ultrasound cavitation occurs. Hence, in-situ measurement method with higher penetration depth in an absorbing liquid is needed to measure and quantify the effect of ultrasound cavitation on the acetic conversion. In this aspect, Synchrotron based FTIR coupled with a special liquid cell for in-situ measurement is essential for such study. We have applied for the synchrotron IR microbeam (B22) using a Harrick FTIR cell and the ultrasound cell for future work

6. Future work and conclusions

In addition to the above proposed synchrotron in-situ FTIR work, the following aspects are proposed to be important for future work in developing ultrasonic catalysis for bio-oil upgrading.

1) Development novel catalysts which work under ultrasonic conditions

2) To find out optimal conditions under while ultrasound works

3) More fundamental understanding/modelling about the reaction steps – find out the controlling reaction steps.

4) Process development to observe the different impacts from the stirring and cavitation of ultrasound application.