Ultrasound sulfonation and esterification for biodiesel production using starch derived heterogeneous acid catalysts

Nathaniel B. Hanson, Mihira Vasana, Bhargavi S. Chilukuri and Ben W.-L. Jang*

Chemistry Department
Texas A&M University-Commerce
Commerce, TX 75429-3011
**corresponding author: ben.jang@tamuc.edu sja@example.edu*

Introduction

Sulfonated carbohydrate derived catalysts from starch, cellulose, sucrose and D-glucose have been widely used in biodiesel production processes as they are low cost. In addition, these materials have been demonstrated to have remarkable catalytic performance for the esterification of free fatty acids [1]. However, Sulfonation of carbon materials typically requires long process time. It's beneficial to cut down the process time and increase acid density on catalysts.

Ultrasound technology has been used to improve biodiesel production. Research done recent showed that ultrasonic techniques can be used to produce favorable reaction results either using a homogeneous or heterogeneous catalyst when producing biodiesel through transesterification of various bio-oils [2]. And, it can be improved on with the use of additional heat and also the use of a high speed rotating stirring mechanism [3]. Ultrasound technique is, therefore, used not only in modifying and improving starch-based catalysts during solfonation but also for oleic acid esterification with methanol in this study.

Experimental Procedures

Laboratory grade starch was pyrolyzed in ultra high purity (UHP) nitrogen at temperatures ranging from 150℃ to 500℃. In the sulfonation procedure, 0.5 grams of carbonated starch is combined with 50 ml of 98 wt. % sulfuric acid in a 50- ml Erlenmeyer flask. The resulting mixture is then introduced to either a heated bath at 150°C or an ultrasound bath. After sulfonation the mixture is filtered then washed flowed by drying at 110°C.

Esterification reactions are carried out using 100 mmol of methanol and 10 mmol of oleic acid with typically 140 mg of catalysts. The reaction mixture can be introduced to either a heated reaction bath or an ultrasonic bath at room temperature. All extractions are analyzed by GC-FID with a Restek MTX-5 column.

Results and Discussion

Catalysts with ultrasonic sulfonation were evaluated for esterification of oleic acid with methanol first. Resulted sulfonated catalysts using ultrasound showed the presence of sulfonic group due to the peak at ~ 1030 cm^{-1}. Ultrasound sulfonation at a frequency of 40 kHz 50W shows a correlation between ultrasound sulfonation duration time and catalyst activity. The longer the ultrasound sulfonation the greater the catalytic esterification activity is. This demonstrates the controllability of the ultrasound procedure.

The effect of ultrasonic sulfonation with different power outputs, including 50W, 60W, and 90W, on catalyst activity were compared. Ultrasounds with higher power are more efficient in sulfonation resulting in higher activity. For example, with 90w, the oleic acid conversion reaches 96% in 120 minutes with three different catalysts.

Ultrasonic catalytic esterification was also evaluated on selected catalysts. As expected, the kinetic of the ultrasonic catalytic esterification is very fast. Higher power ultrasounds are also more effective for esterification. For example, the conversion with power of 90W reaches to more than 99% within 10 minutes of reactions on three different catalysts, as shown in Table 1.

Table 1. Conversion results of ultrasonic esterification with 42 kHz & 90W over catalysts.

	Reaction Time (in minutes)			
	10	**20**	**30**	**60**
300C15H 150S15H	99.1%	98.9%	99.1%	99.8%
200C4H US8H	99.7%	99.6%	99.8%	99.9%
200C4H150S15H	94.3%	95.6%	99.8%	99.9%
400C15H US8H	99.1%	99.3%	99.6%	99.9%

Catalyst reusability was tested by using one of the best catalysts, 200C4H US4H (200°C pyrolysis for 4 hours followed by ultrasonic sulfonation for 4 hours), for multiple reactions. In order to see the decrease within reasonable time frame, 30 mg of catalysts was used. The catalyst activity remains stable in the 2nd cycle. However, the activity dropped quickly in the 3rd and 4th cycles.

Table 2. Stability test of 200C4H US4H for ultrasound esterification.

	Reaction Time (in minutes)				
	5	**10**	**20**	**30**	**60**
30 mg	40.8%	69.5%	70.6%	92.8%	92.9%
Run #2 28.3mg	39.6%	65.7%	76.8%	90.3%	90.3%
Run #3 26.5mg	30.1%	47.8%	65.7%	65.7%	70.3%
Run #4 22.5 mg	10.6%	10.8%	9.8%	10.7%	10.9%

Significance

Ultrasonic catalytic esterification was very effective, achieving 99% conversion within 10 minutes, the activity is much higher but follows the same degrading trend. The recycling stability of 200C4H US4H was very good for the 2nd cycle, but decreased relatively quickly in the 3rd & 4th cycles.

Reference

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