



## Optimization of free fatty acid reduction in coconut oil via sulfamic acid-catalyzed esterification

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### ABSTRACT

This study presents the two-step esterification process for the reduction of free fatty acid (FFA) content in coconut oil to less than 1% w/w. The initial value of FFA content in coconut oil was 25.22% w/w. The esterification reaction in the presence of sulfamic acid as a catalyst was carried out to investigate the optimum conditions and to study the effects of variables on the reaction. These variables included methanol contents of 20-50% v/v, catalyst amounts of 0-15% w/v of oil, reaction temperatures of 25-60 °C, and reaction times of 1-4 h. The FFA content in oil was determined by AOAC Official Method 940.28 (AOAC 2012). After the two-step process, the FFA content was reduced to 0.91% w/w. The optimum conditions for the first step were a methanol content of 50% v/v, catalyst amount of 10% w/v of oil, a reaction temperature of 60 °C, and a reaction time of 2 h. The optimum conditions for the second step were a methanol content of 40% v/v, catalyst amount of 5% w/v of oil, a reaction temperature of 60 °C, and a reaction time of 2 h. In addition, the results demonstrate that all of the reaction variables had the positive effects on the reaction.

**Keywords:** Free fatty acid, Esterification, Sulfamic acid, Coconut oil

### 1. INTRODUCTION

The fact that nowadays petroleum is very important in human life and it is the major world energy resource. It is used as fuel in transportation, industry, household, electricity generation, and agriculture. Besides, petroleum is comprised of a mixture of various hydrocarbons which can be used as feedstock in petrochemical industry. However, petroleum resource is limited and non-renewable and the global petroleum use as fuel has had a negative impact on the environment such as global warming and air pollution. In the present day, Thailand strongly relies on crude oil import and it resulted in the costs huge expenditure of the country. Therefore, in order to relieve these problems, the alternative fuel must be used. One of the interested alternative fuels was biodiesel which is renewable, environmental friendly, and available locally. Biodiesel is the fatty acid methyl ester which is produced currently from plant oils and animal fats. In many countries, biodiesel is produced from plant oils such as soybeans, canola

oil, palm oil, corn oil, coconut oil, and jatropha oil. In addition, the used cooking oil is the high potential commercial source for biodiesel production.

In general, the crude and waste vegetable oils are more viscous than petroleum diesel for many times. For example, the viscosity of Stone fruit kernel oil and waste coffee oil are 34.82 and 26.74 mm<sup>2</sup>/s at 40 °C, respectively [1,2] while the viscosity of Thai petroleum diesel is 1.8-4.1 mm<sup>2</sup>/s at 40 °C (ASTM D 445). Therefore, the use of vegetable oil in an unmodified diesel fuel system will cause the negative effects to the engine and fuel system such as poor fuel atomization, incomplete combustion, and coking of the fuel injectors. In order to solve these problems, the vegetable oil must be transesterified to acquire a viscosity close to that of petroleum diesel. Nowadays, the commercial process for biodiesel production is alkali-catalyzed transesterification in which triglyceride in oil and fat are converted to methyl ester (biodiesel) and glycerol. The feedstocks for this process are vegetable oils and



animal fats containing free fatty acid (FFA) less than 1% w/w [3]. However, these feedstocks are expensive. Thus, the low price feedstocks such as oils and fats having FFA content more than 1% w/w should be used instead to reduce the biodiesel production cost. However, the high FFA content is the obstacle in the alkali-catalyzed transesterification because FFAs react with alkaline catalyst to form soap. Soap increases the viscosity of the reaction mixture resulting in the lower yield of biodiesel. In addition, soap inhibits the separation of biodiesel from glycerol and washing water. Therefore, to solve this problem, the two-step process for biodiesel production was used. The first step is the pretreatment step in which the FFAs in oil are esterified to methyl esters by using acid catalyst and the FFA content is reduced to less than 1% w/w after the reaction. In the second step, triglycerides in oil are transesterified to biodiesel by using alkaline catalyst. In esterification step, sulfuric acid is the most commonly preferred homogeneous catalyst. Although sulfuric acid has high efficiency to catalyze esterification, it has some disadvantages such as corrosivity, a large amount of water is used to wash the product, and a large amount of waste water needs to be treated. With these reasons, many researchers currently aim at the use of heterogeneous catalysts such as Lignin-based solid acid catalyst manufactured from olive cake [4], Montmorillonite Clay K-30 [5], and Zirconia-supported tungstophosphoric heteropolyacid [6] in biodiesel production. In addition, some researchers reported the success of use sulfamic acid as eco-friendly catalyst to convert FFAs in oil to alkyl esters via esterification [7].

Sulfamic acid (SA,  $\text{NH}_2\text{SO}_3\text{H}$ ) is a white crystalline solid, odorless, and relatively stable. It is moderately soluble in water and slightly soluble in methanol. In recent year, reports in the literatures revealed the several advantages of using sulfamic acid as catalyst in organic synthesis, including non-hygroscopicity, non-corrosivity, non-volatility, easy separation from the reaction mixture and reusable, and low cost [8,9]. Hence,

in this study the researchers focus on the reduction of FFA content in coconut oil containing high FFA via acid-esterification. The coconut oil is one of the high potential feedstocks for biodiesel production in Thailand. The objectives of this study were: (a) To investigate the optimum reaction conditions for the reduction of FFA in coconut oil to less than 1% w/w by using sulfamic acid-catalyzed esterification, and (b) To study the effects of the important variables on the reaction.

## 2. MATERIALS AND METHODS

The coconut oil feedstock was obtained from Sangsook Industry Company Limited as unrefined types. Absolute ethanol was purchased from Merck. Potassium hydrogen phthalate, sulfamic acid, phenolphthalein, and sodium hydroxide were purchased from Ajax Finechem Pty Ltd. All chemicals used in this study, such as absolute ethanol, phenolphthalein, sulfamic acid, sodium hydroxide, and potassium hydrogen phthalate were analytical grade.

### Preparation of coconut oil

The coconut oil was viscous, amber color and had suspended solid particles. The oil was heated at 60 °C and subsequently filtered to remove impurities with Whatman filter paper No.93. After that, the free fatty acid in coconut oil was determine by AOAC Official Method 940.28 (AOAC 2012). Besides, some physical properties of coconut oil such as viscosity, density, and water content were also tested by standard test methods.

### Apparatuses

The apparatuses used for acid-catalyzed esterification of FFA in coconut oil consisted of a 250 mL three-necked flat-bottom flask as reactor and hotplate with a magnetic stirrer. The two necks of the reactor were equipped with a reflux condenser and thermometer while the other neck was used for sulfamic acid feeding. The reflux condenser was used to condense the evaporated methanol back to the reaction mixture.



**Experimental conditions**

In this study, the sulfamic acid-catalyzed esterification was performed with the aim of investigating the optimum conditions for the reduction of FFA content in coconut oil to less than 1% w/w and to study the effects of dominant variables on the reaction. The reduction process composed of two steps and it was carried out at the atmospheric pressure in a laboratory-scale experiment. In the first step, the dominant variables affecting the esterification such as methanol amounts (20, 30, 40, and 50% v/v), catalyst amounts (0, 5, 10, and 15% w/v of oil), reaction temperatures (25, 40, 50, and 60 °C) and reaction times (1, 2, 3, and 4 h) were optimized. In the second step, methanol amounts of 30 and 40% v/v were used to investigate the optimum condition to reduce the FFA content in coconut oil to less than 1% w/w.

**Experiment**

The coconut oil feedstock, methanol, and sulfamic acid were used in amounts of established for each experiment. The coconut oil was first charged into the reactor and heated to the desired temperature. Then, methanol and sulfamic acid was added to the preheated oil. After the completion of the addition, the time was considered as the beginning of the experiment. The reaction mixture was heated and stirred at constant stirring speed until the end of the reaction time. After the reaction, the reaction mixture was poured into separatory funnel and allowed to settle overnight under gravity to separate methanol, spent catalyst and water produced during the reaction. The reaction mixture was separated into two layers. The top layer consisted of coconut oil, trace unreacted methanol and water whereas the lower layer contained a mixture of an excess of unreacted methanol, catalyst, and water. The oil layer was separated and then subjected to remove water and residual methanol by heating at 110 °C. After that, the impurities in oil was removed by filtration with Whatman filter paper No.93 and the clear oil product was obtained. Finally, the content of unreacted FFA which remained in oil product was

determined by AOAC Official Method 940.28 (AOAC 2012).

**3. RESULTS AND DISCUSSION**

**Characterization of the coconut oil**

The coconut oil used in this study was clear, viscous and amber color after filtration. Its some important properties are shown in Table 1.

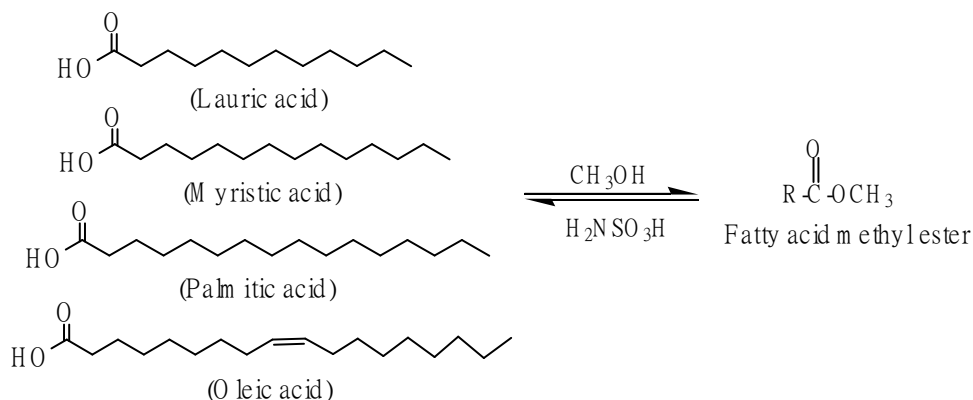
**Table 1.** Properties of coconut oil feedstock

Property	Method	Oil
FFA content, % w/w	AOAC 940.28 (AOAC 2012)	25.22
Kinematic viscosity at 40 °C, mm <sup>2</sup> /s	ASTM D 445	29.23
Density at 15 °C, kg/m <sup>3</sup>	ASTM D 4052	0.9256
Water content, % w/w	ASTM E 1064	0.666

Coconut oil is more viscous than Thai petrodiesel about ten times and it has low volatility. Therefore, it is not suitable for direct use in a unmodified diesel engine because it causes the difficulty in fuel atomization and in mixing of fuel and air. To improve the coconut oil performance in diesel engine, its viscosity must be reduced to a level close to petrodiesel. The best way to achieve this purpose is converting coconut oil to biodiesel. The initial FFA content of coconut oil was 25.22% w/w and this value is beyond the limited value (1% w/w) of oil used as feedstock for biodiesel production. Therefore, it is difficult to convert this oil to biodiesel by commercial alkali-catalyzed transesterification process due to the soap formation. From this reason, the researchers used the two-step esterification process to reduce the FFA content in coconut oil to less than 1% w/w. The coconut oil contained trace of water so it was not a obstacle for the esterification reaction.

Coconut oil is the mixture of saturated, monounsaturated and polyunsaturated fats. The saturated fat in coconut oil is made up of six different types of fatty acids, including caprylic, capric, lauric, myristic, palmitic, and stearic acid. Of the six types of fatty acid, the most predominant is lauric acid. The monounsaturated and polyunsaturated fat in coconut oil are made entirely of





Scheme 1. Esterification reaction of FFAs

oleic acid and linoleic acid, respectively. The fatty acid composition of coconut oil was shown in Table 2.

**Table 2.** Fatty acid composition of coconut oil [10]

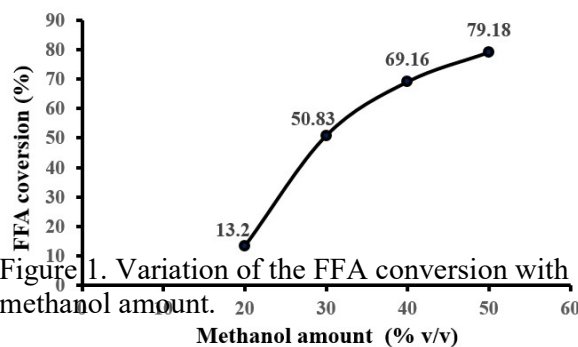
Fatty acid	Fatty acid content (%)
Caprylic acid (C8:0)	3.35
Capric acid (C10:0)	3.21
Lauric acid (C12:0)	32.72
Myristic acid (C14:0)	18.38
Palmitic acid (C16:0)	13.13
Stearic acid (C18:0)	3.60
Oleic acid (C18:1)	12.88
Linoleic acid (C18:2)	4.35

Hence, during sulfamic acid-catalyzed esterification, the FFAs were esterified to form various kinds of methyl esters of fatty acids such as methyl laurate, methyl myristate, methyl palmitate, and methyl oleate as shown in Scheme 1.

**Acid-catalyzed esterification : Step 1**  
**The effect of methanol amount**

Esterification requires 1 mole of methanol for each mole of fatty acid to produce 1 mole of methyl ester and 1 mole of water. The reaction is an equilibrium and the using of large excess of methanol ensures that the reaction is driven to methyl esters direction. Therefore, one important variable affecting the esterification is the methanol amount. In this study, the effect of methanol amounts of 20, 30, 40, and 50% v/v (1:4, 1:7, 1:11, and 1:17 molar ratio of FFA/methanol, respectively)

on the esterification was investigated at the conditions of 5% w/v of oil sulfamic acid catalyst, 60 °C, and 2 h of reaction time. The results were shown in Figure 1.



**Figure 1.** Variation of the FFA conversion with methanol amount.

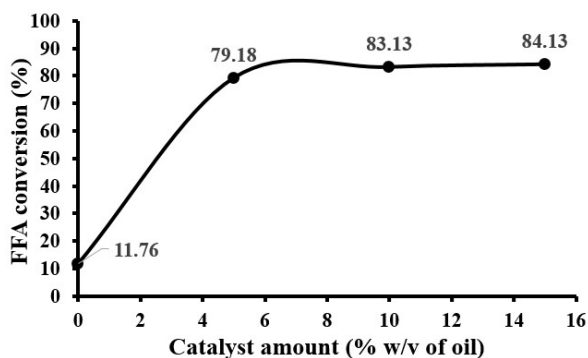
**Figure 1** shows that the methanol amount significantly affects the FFA conversion. When the methanol amount was 20% v/v (1:4 molar ratio of FFA/ methanol), the FFA conversion was only 13.2%. The FFA conversion increased rapidly from 13.2-79.18% with an increasing of methanol amount from 20%-50% v/v. The same trend was reported by Montes D'Oca, M.G. et al.[8]. A maximum FFA conversion was reached at 50% v/v. (1:17 molar ratio of FFA/methanol) and the FFA content in oil was reduced to 5.25% w/w at this point. The increase in FFA conversion trend



can be explained by Le Chatelier's principle. When methanol amount increased, the equilibrium shifted in the direction of forward reaction. This led to the increasing of methyl ester and water formation. Furthermore, the viscosity of the reaction system reduced when the large excess of methanol was used. This resulted in the better mixing between oil, methanol, and catalyst which promoted the rate of reaction. Hence, the FFA conversion was increased rapidly in the fixed reaction time. Therefore, the optimum methanol amount was 50% v/v and the investigation of the effect of catalyst amount was conducted by using this methanol amount.

#### The effect of catalyst amount

Another important variable that affects the acid-catalyzed esterification is the catalyst amount. To investigate the effect of catalyst amounts (0, 5, 10, and 15% w/v of oil) on esterification, the experiments were carried out at the condition of methanol amount of 50% v/v, 60 °C, and 2 h. The results were shown in Figure 2.



**Figure 2.** Variation of the FFA conversion with catalyst amount.

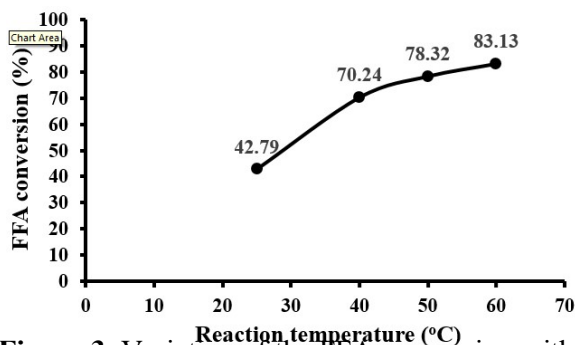
It can be seen clearly from Figure 2 that the minimal FFA conversion of 11.76% was obtained when sulfamic acid was not used as catalyst. The esterification could have occurred from the autocatalysis whereby the reaction was catalyzed by the FFA in coconut oil. The rate of reaction was increased considerably in the presence of sulfamic acid and resulting in the high FFA conversion. These results indicated that sulfamic acid had the

important role as catalyst for the esterification of FFA in coconut oil with methanol. Increasing the catalyst amount increased the reaction rate. Hence, at catalyst amount of 5% w/v of oil provide FFA conversion of 79.18% (FFA content 5.25% w/w) within 2 h, whereas 10% w/v of oil provide FFA conversion 83.13% (FFA content 4.25% w/w) in the same reaction time. The same results were observed by Montes D'Oca, M.G. et al. who studied the efficiency of sulfamic acid as catalyst for the esterification of oleic acid and the results showed that an increase in catalyst amount from 5 to 10% increased methyl oleate yield from 71 to 80% under the condition of molar ratio of methanol/oleic acid of 6:1 and 120 °C [8]. However, the gradual decrease in esterification rate was observed when the catalyst amount beyond 5% w/v of oil was used and the reaction slowly reached its equilibrium after methanol amount of 10% w/v of oil. From an economical point of view, 5% w/v of oil was selected as the optimum catalyst amount and this value was used to investigate the effect of reaction temperature. In the industrial scale, sulfamic acid in the methanol-water layer can be recovered and recycled.

#### The effect of reaction temperature

In this study, the effect of reaction temperatures (25, 40, 50, and 60 °C) on sulfamic acid-catalyzed esterification were investigated at the conditions of methanol amount of 50% v/v, catalyst amount of 5% w/v of oil and the reaction time of 2 h. The results were shown in Figure 3.

Esterification is the endothermic reaction so heat is needed to drive the reaction to the product side [11]. Figure 3 reveals that sulfamic acid-catalyzed esterification of FFA in coconut oil with methanol could occur at different temperatures, even though at room temperature (25 °C) but the reaction is incomplete. Rate of sulfamic acid-catalyzed esterification increased with increasing reaction temperature. This resulted in the increasing of FFA conversion consecutively. It can be explained by the four reasons. First, esterification is the endothermic reaction. Thus, when the temperature



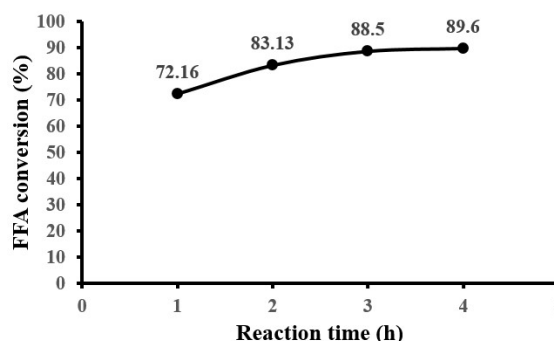
**Figure 3.** Variation of the FFA conversion with reaction temperature.

increased, the rate of reaction increased. Second, as the temperature increased, the reactant particles had higher energy. They moved more quickly and more of the collisions which resulting in the increasing rate of reaction. Third, from the mass transfer perspective, coconut oil was not soluble in methanol but the solubility of oil increased when the reaction temperature increased. This lead to the lesser resistance to mass transfer which resulted in more completion of the reaction. The last reason, by increasing of reaction temperature, the viscosity of coconut oil decreased resulting in the better mixing between oil, methanol and catalyst. This lead to the more conversion of FFA to methyl ester. This trend was also observed by Montes D'Oca, M.G. et al. who studied the effect of reaction temperature on the esterification of oleic acid. They reported that when the reaction temperature of 80, 100, and 120 °C were used, the yields of methyl oleate were 62%, 76%, and 80% respectively [8].

The FFA conversion reached the maximum value of 83.13% at 60 °C and the FFA content was reduced to 4.25% at this point. In this study, in order to avoid an excessive loss methanol, the effect of reaction temperatures beyond 60 °C were not investigated due to the boiling point of methanol was 64 °C. Therefore, 60 °C was selected as the optimum reaction temperature and it was used to investigate the effect of reaction time.

### The effect of reaction time

To investigate the effect of reaction times (1, 2, 3, and 4 h) on sulfamic acid-catalyzed esterification, the experiments were carried out at methanol amount of 50% v/v, catalyst amount of 5% w/v of oil, and reaction temperature was 60 °C. The results were shown in Figure 4.



**Figure 4.** Variation of the FFA conversion with reaction time.

The results indicated that the conversion rate was so high in the first one hour. This is due to the water content was minimal in that period of time. As the esterification proceed, the formation of water increased resulting in the hydrolysis of methyl ester back to FFA. Therefore, the rate of reactions were reduced consecutively when the reaction times increased from 2 to 4 h. The esterification reached it equilibrium after 3 h and in these periods of time, the rate of methyl ester formation equaled the rate of hydrolysis of methyl ester. Hence, from an economical point of view, 2 h was selected as the optimum reaction time.

Therefore, the optimum conditions obtained from the step 1 were methanol amount of 50% v/v, catalyst amount of 5% w/v of oil, reaction temperature of 60 °C and reaction time of 2 h. At this condition, FFA conversion was 83.13% and the FFA content was reduced from initial value to 4.25% w/w.

### Acid-catalyzed esterification : Step 2

In order to investigate the optimum condition for the reduction of FFA in coconut oil to less than 1% w/w, the coconut oil having FFA content





4.25% w/w was produced by using the optimum condition in Step 1. After that, the produced oil was used to further investigate. The investigation was conducted by variation of methanol amount (30 and 40% v/v) under the conditions of catalyst amount of 5% w/v of oil, reaction temperature of 60 °C, and reaction time of 2 h. The results were shown in Table 3.

**Table 3.** Esterification of FFA in step 2

Methanol amount (% v/v)	FFA content in oil (% w/w)
30	1.58
40	0.91

From Table 3., it indicated that the FFA content in coconut oil was reduced to less than 1 %w/w at the methanol amount of 40% v/v. Therefore the optimum condition for step 2 was methanol amount of 40% v/v, catalyst amount of 5% w/v of oil, reaction temperature of 60 °C, and reaction time of 2 h. At this point, the FFA was reduced from initial value to 0.91% w/w.

#### Properties of oil product

The oil product having FFA content 0.91% w/w was produced by the two-step acid-catalyzed esterification process and it was sent to the Bangchak Petroleum Public Company Limited for the properties testing. The results were shown in Table 4.

**Table 4.** Properties of oil product

Property	Method	Oil product
Kinematic viscosity at 40 °C, mm <sup>2</sup> /s	ASTM D 445	15.62
Density at 15°C, kg/m <sup>3</sup>	ASTM D 4052	0.9159
Water content, % w/w	ASTM E 1064	0.097

The results showed a significant viscosity reduction from 29.23 to 15.62 mm<sup>2</sup>/s after the two-step acid-catalyzed esterification. This obviously indicated that sulfamic acid catalyzed both esterification and transesterification in the same time. The sulfamic acid-esterification converted FFA to methyl ester and water while sulfamic acid-transesterification converted triglyceride to methyl ester and glycerol. However,

the acid-catalyzed transesterification of triglyceride occurs slowly and it is slower than alkali-catalyzed transesterification of triglyceride about 4,000 times [12]. The oil viscosity was reduced by a half after the reaction because the high molecular weight triglyceride was transesterified to the low molecular weight fatty acid methyl ester. The oil product contained minute traces of water and this confirmed that the water removing process in this study was efficient.

#### 4. CONCLUSIONS

This study reveals that the FFA content in coconut oil can be reduced to less than 1% w/w by the two-step process sulfamic acid-catalyzed esterification with methanol. In the first step, the optimum conditions were methanol amount of 50% v/v, catalyst amount of 10% w/v of oil, reaction temperature and reaction time of 60 °C and 2 h respectively. At this condition, the FFA content was reduced from the initial value of 25.22 to 4.25% w/w (83.15% FFA conversion). In the second step, the FFA content was reduce to 0.91 % w/w by using methanol amount of 40% v/v, catalyst amount of 5% w/v of oil, reaction temperature of 60 °C, and reaction time of 2 h. All of the variables such as methanol amount, catalyst amount, reaction temperature, and reaction time had the positive effect on the sulfamic acid-catalyzed esterification. The information obtained from this study will be useful to biodiesel producer for produce biodiesel from low cost coconut oil containing significant amounts of free fatty acid. It is the suitable process as a pretreatment step for coconut oil having free fatty acid content between 1-25.22% w/w).

#### 5. ACKNOWLEDGMENTS

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