

# PRODUCTION OF BIODIESEL FROM EXTRACTS OF SUMAC (*RHUS TYPHINA*) FRUIT CLUSTERS

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Sumac (*Rhus typhina*) fruit clusters were extracted with acetone/water (9:1, v/v) and 1% sodium hydroxide, respectively, for the preparation of biodiesel. The product was compared with biodiesel from vegetable oil and evaluated to determine if the sumac could be used as an alternate biodiesel resource. Parameters such as the amount of accelerator required, the length of reaction time and pH were evaluated based on the production. The biodiesel yields reached 12% (w/w) based on the acetone/water extract. The characteristics of sumac biodiesel present no significant difference from those of commercial diesel.

**Keywords:** sumac, acetone/water extract, 1% sodium hydroxide extract, biodiesel

## INTRODUCTION

The generation of renewable energy as biodiesel fuels requires a steady supply of raw materials. Currently, the most common materials used for biodiesels are vegetable, waste vegetable oils and animal fats (tallow),<sup>1-3</sup> however the supply of these materials is not sufficient. Because of this limitation, it is necessary to investigate new alternative fuel sources from our environment. We have recently reported on the use of tall oil, a kraft pulping by-product, as a biodiesel resource.<sup>4</sup> However, most kraft pulping mills have almost completely systemized the procedure, including the black liquor. Without adding special extra value to the product from tall oil, no one would change the already systemized pulping process. The black liquor is a very important energy source in a kraft mill. If the black liquor is removed from the pulping system in order to be used for biodiesel, the mill will have to find another energy source. Therefore, it is difficult to expect the tall oil in kraft mills to be considered as a viable raw material for biodiesel.

In this study, we generate biodiesel from sumac fruit clusters and investigate their possibility for biodiesel production. Sumac trees are distributed in the subtropical and temperate regions of the world, especially in Africa and North America. They are shrubs and small trees that can reach a height of 1-10 m.<sup>5</sup> The fruit of the

*Rhus* genus are ground into powder and used as a spice in Middle Eastern cuisine, adding a lemony taste to salads or meat.<sup>6</sup> In Arab cuisine, the spice is used as a garnish on *meze* dishes, including *hummus* and *tashi*, and it is added to salads in the Levant region. It is also used to make tea by boiling the dried leaves.<sup>7</sup>

In North America, the smooth sumac (*Rhus glabra*) and the staghorn sumac (*Rhus typhina*) are sometimes used to make a beverage called “sumac-ade”, “Indian lemonade” or “rhus juice”. This drink is made by soaking the fruit clusters in cool water and rubbing them to extract the essence.<sup>8</sup>

The culinary uses of sumac, spices and drinks, consume only a minor amount of the available plants, and its large availability allows developing additional uses for the plant. In addition, sumac was reported to be an oily plant in China,<sup>9</sup> thus, we attempted to make biodiesel from sumac fruit clusters, thinking that they are a viable alternative and sustainable biofuel resource.

## EXPERIMENTAL

### Materials

Staghorn sumac (*Rhus typhina*) fruit clusters were harvested in mid-October, air dried and stored in the laboratory (moisture content 4.1%). Acetone, methanol, sodium hydroxide (93%), sulfuric acid (72%), acetyl

chloride were all purchased from Sinopharm Chemical Reagent Co., Ltd.

#### **Extraction of sample**

##### ***Extraction of sample by acetone/water (9:1 v/v) mixture<sup>10</sup>***

The density of sumac fruit clusters is very low. In order to obtain a good extract with the solvents, sumac fruit clusters (500 g) were divided into two 250 g portions. Each of them was placed in a 2 liter Erlenmeyer flask and extracted three times with one liter of acetone/water (9:1, v/v) mixture under sonic vibration for one hour. After each run, the acetone/water mixture was replaced with a fresh one. In the third extraction, it was left overnight at room temperature. The next day, the extract was filtered with a Buchner funnel without filter paper and was washed with fresh acetone/water mixture 3 times. The filtrate and washings were combined and concentrated by a rotary evaporator (the yield of extracts: 83.2 g, 16.9%, w/w; the solvent recovery rate: 65.0%, w/w).

##### ***Extraction of sample by sodium hydroxide***

Sumac fruit clusters (500 g) were divided into two 250 g portions. Each of them was placed in a 2 liter Erlenmeyer flask and extracted three times with one liter of 1% sodium hydroxide aqueous solution under sonic vibration for one hour. After each run, the 1% sodium hydroxide solution was replaced with a fresh one. After the third extraction, it was left overnight at room temperature. The next day, the extract was filtered with a Buchner funnel without filter paper and was washed three times with hot water. The filtrate and washing liquor were combined and concentrated by a rotary evaporator (the yield of extracts: 242.8 g, 49.2%, w/w).

#### **Esterification of extracts**

##### ***Esterification of acetone/water extracts***

The sample extracted by the acetone/water mixture was suspended in 400 mL of methanol. Then, 30 mL acetyl chloride was slowly added to the suspension at room temperature, after which the reaction mixture was heated with a stopper under 100 r/min stirring at 55 °C for one hour. After cooling down, the reaction mixture was concentrated and the methanol was recovered by a rotary evaporator (recovery rate: 85.0%). The residue was dissolved in 400 mL of ethyl acetate and transferred to a 1000 mL separatory funnel and washed with 200-300 mL of water for 3 times. At this point, the pH was measured for the first washing water.<sup>11</sup> The organic layer was dried with anhydrous sodium sulfate and was concentrated into a 250 mL round bottom flask and the ethyl acetate was recovered (recovery rate: 65.0%) by a rotary evaporator.

##### ***Esterification of sodium hydroxide extracts***

The sample extracted by sodium hydroxide was suspended in 500 mL methanol, then 50 mL acetyl

chloride was added under stirring at room temperature. After this, the reaction mixture was heated with a stopper under stirring at 55 °C for one hour. After cooling down, the reaction mixture was concentrated and the methanol was recovered by a rotary evaporator (recovery rate: 85.0%). The residue did not dissolve in ethyl acetate as it usually does, therefore it was treated by sonic vibration with 500 mL of ethyl acetate for one hour three times. At this point, a small amount of sample was mixed in water and the pH was measured. Each time, the solvent was replaced with a fresh one. After the third extraction, it was left overnight and filtrated on the next day. The three extracts were combined and dried with anhydrous sodium sulfate. After filtration, the extract was concentrated into a 250 mL round bottom flask and the solvent was recovered by a rotary evaporator (recovery rate: 85%).

#### **Vacuum distillation**

Each concentrate obtained as described above in 250 mL round bottom flasks was subjected to vacuum distillation and the liquid fraction with the boiling point ranging between 150 and 190 °C (2 mmHg) was collected as biodiesel fuel.

#### **Analysis of biodiesel by gas chromatography**

The biodiesel sample (extracted by the acetone/water solvent), refined as described above, was analyzed by gas chromatography using a Hewlett Packard Model 5890 GC with an attached capillary column (EC-1, 30 m × 0.25 mm, Alltech Corp.). The operating conditions were as follows: injector temperature: 150 °C, detector temperature: 270 °C, initial temperature: 80 °C, holding time: 1 min, increment rate: 2 °C/min, final temperature: 250 °C, holding time: 5 min. Biodiesel prepared from vegetable oil was also analyzed under these conditions to be compared with the samples obtained from the sumac fruit clusters. As the yield of the biodiesel sample extracted by 1% NaOH was low, after the first step of yield comparison, all the measurements (GC and quality indexes of biodiesel) are reported only for the sample extracted by the acetone/water (9:1, v/v) solvent.

#### **Measurement of quality indexes of biodiesel**

There are a number of standards to assess the quality of biodiesel fuels, for example, EN14214:2003 (Europe), DINV51606 (Germany), ASTM D 6751-07b (USA), and EN590:1999, GB/T20828-2007(China). Indeed, engine manufacturers and biodiesel plants use slightly different standards for biodiesel quality depending on region. In this paper, we measured the density, 90% recovery temperature, and clarity number as per the GB/T standards, while the kinematic viscosity, flash point, carbon residue, cetane number, acid value and water percent were measured using the ASTM standard. All the measurements were carried

out by the Shanghai Microspectrum Chemical Technology Service Co., Ltd. in China.

## RESULTS AND DISCUSSION

### Yield of extraction and biodiesel

The yield of biodiesel is shown in Table 1. Compared to tall oil and soap skimmings, the sumac extractives contained a large amount of impurities, including flavonoids, gallic acids and antioxidant-related compounds.<sup>12</sup> During the process of esterification, fatty acids and resin acids were converted to target materials. Both of these were present in the reaction mixture and were converted into acid esters, which were collected by distillation. The yield of biodiesel was 12.23% w/w, based on the acetone/water extract, and 2.02% w/w, based on the raw material (the mass of the fruit clusters). On the other hand, the yield of the biodiesel from the extract obtained with 1% sodium hydroxide was 3.95% w/w based on 1% alkali extract and 1.94% w/w based on the raw materials (the mass of fruit clusters). From these results, 1% sodium hydroxide extraction was very efficient (49.24% w/w, 3 times greater than the acetone/water extraction), but the yield of biodiesel was low (3.95% w/w, 1/3 of acetone/water extract). The 1% sodium hydroxide extract had a very high

yield (49.24% w/w), but the total amount of the final biodiesel product, based on the cluster mass, was basically the same (2% w/w) when comparing the two methods. This means that the increased extract by the sodium hydroxide is not beneficial for the final product. It is likely that the 1% sodium hydroxide extraction was more efficient due to the large amount of gallic acid and related acidic materials, but not fatty acids in the clusters.

Based on the above discussion, the acetone/water extraction method is a better choice for obtaining biodiesel because it requires less total reaction materials (extracts), as well as less solvent and chemicals. It is also a more simplified and time efficient procedure.

### GC (gas chromatography) data

The sumac biodiesel product was tested by GC using the same conditions that were used for vegetable oil and tall oil.<sup>4</sup> The composition of the sumac and vegetable oil samples were similar, showing methyl palmitate (MP), methyl linoleate (ML), methyl oleate (MO), and methyl stearate (MS). The yield and composition data are shown in Table 2.

Table 1  
Yield of biodiesel from different sources

	MeOH (mL)	AcCl (mL)	Temp. (°C)	Time (h)	Yield (%)
Sumac A/W ext.*	400	30	55	1	12.3
Sumac NaOH ext.*	400	30	55	1	3.9
Vegetable oil	400	30	55	1	74.6
Crude tall oil	400	30	55	1	55.6
Soap skimmings	400	30	55	1	37.5

\*Sumac A/W ext. – acetone/water extracted sumac; Sumac NaOH ext. – 1% NaOH extracted sumac

Table 2  
Sumac and vegetable oil biodiesel components and their relative content

Component	Molecular formula	Retention time (min)		Relative content (%)	
		SB*	VOB*	SB	VOB
Methyl palmitate	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	41.41	41.12	26.97	11.15
Methyl linoleate	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	48.65	49.09	4.59	58.08
Methyl oleate	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	49.55	49.51	53.77	25.35
Methyl stearate	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	50.66	50.53	6.17	4.22

\*SB – sumac biodiesel; VOB – vegetable oil biodiesel

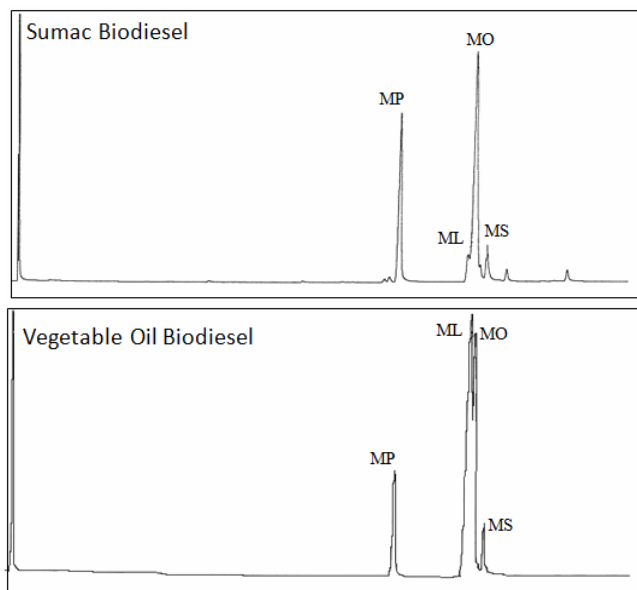


Figure 1: Gas chromatogram of biodiesel from sumac acetone/water extract (upper) and vegetable oil (lower); (MP: methyl palmitate, ML: methyl linoleate, MO: methyl oleate, MS: methyl stearate)

Table 3  
Quality indexes of sumac biodiesel *versus* commercial diesel

Index	Method	Sumac biodiesel (A/W extracted)	GB/T20828	Commercial diesel
$\rho$ (20°C)/(g/cm <sup>3</sup> )	GB/T2540	0.879	0.82~0.90	0.90
Kinematic viscosity $\mu$ (40 °C)/(cm <sup>2</sup> /s)	ASTM/D445	6.87	1.9~6.0 (20°C)	3.0~8.0 (20°C)
Flash point (°C)	ASTM/D93	165	≥130	≥55
Carbon residue (10% dist. residue)	ASTM/D4530	<0.3	<0.3	<0.3
Cetane number	ASTM/D613	≥49	≥47	≥49
Acid value KOH/(mg/g)	ASTM/D664	0.21	≤0.8	<7
90% recovery temperature	GB/T6536	270	360	<355
Clarity number	GB/T260-1986	1.3	-	≤3.5
Water (%)	ASTM/D2709	0.001	≤0.5	Trace

The data suggest that the fatty acids in the plant can be quantitatively converted into the corresponding fatty acid esters, despite the presence of salts and other impurities. The chromatograms comparing the sumac and vegetable biodiesel samples are shown in Figure 1. In the sumac biodiesel samples, methyl oleate (53.77%) was the primary component and methyl palmitate (26.97%) was a secondary one; while in vegetable oil biodiesel, methyl linoleate (58.08%) was the primary component and methyl oleate (25.35%) was the secondary.

#### Biodiesel characterization

Table 3 details the density, kinematic viscosity, flash point, 10% carbon residue on residuum,

cetane number, acid value, 90% recovery temperature, clarity number, and water content measured in the sumac sample and commercial diesel samples. The sumac biodiesel showed very similar values compared to the commercial diesel, indicating that the biodiesel obtained by this method could be mixed with commercial diesel for use. In addition, it would be possible to use the biodiesel obtained by this method as the only energy source in diesel engines or boilers. Biodiesel contaminants vary depending on the source materials and the extraction method used. Based on the boiling point and GC chromatography data, sumac fruit clusters were found to be a suitable raw material to generate biodiesel. Also, considering that the plant is not a

major part of the food supply chain increases its potential as a viable alternative source of biofuel. Vegetable oil based biodiesel, tall oil based biodiesel and sumac based biodiesel have very similar properties all within the acceptable ranges, however they show some differences due to the different raw materials and methods used for extraction.

## CONCLUSION

Our results revealed that sumac fruit clusters can be used as a raw material to produce biodiesel. The yield was 12% w/w using the acetone/water extraction method. The characteristics of the sumac biodiesel were not significantly different from those of the vegetable oil based fuel. This study will be of significance in developing industrial applications using sumac fruit clusters as a novel material for the generation of biodiesel. By the method developed in this study, the extracts can be converted into biofuels, while the residues, including celluloses, hemicelluloses and lignins, could be used as raw materials for further bio-refinery. All the organic solvents used in both extraction and esterification steps can be recycled, the process will be eco-friendly when it is used on an industrial scale.

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