Production of Biodiesel Using a Vegetable Oil from *Swida wilsoniana* Fruits

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Abstract

Energy demand is increasing dramatically due to the fast industrial development, rising population, expanding urbanization, and economic growth in the world and large amount of fossil fuels are widely used. The depletion of fossil fuel reserves and the environmental pollution caused by burning of fossil fuels stimulate development of alternative fuels. Biodiesel today is the most popular and promising biofuel and vegetable oils are one of the potential feedstocks for biodiesel production. In order to explore the wild oil plant sources in China, the fruit oil of Swida wilsoniana, a wild woody oil plant widely distributed in the mountainous regions of calcareous sandstone, was used to produce the biodiesel by transesterification method. The reaction parameters were optimized by an orthogonal experimental design. The results showed that Swida wilsoniana fruit oil (SWO) could be conversed to biodiesel at a wide range of reaction conditions. The optimum conditions for the reaction process were determined as: methanol/oil mole ratio 5:1, catalyst dosage 1.1%, reaction temperature 60 °C, and reaction time 120 min. The characteristics of Swida wilsoniana biodiesel (SDBD) were analyzed, which was similar to that of 0# diesel. Moreover, SDBD has the advantages of higher flash point (>105) and lower ash content (<0.003). Therefore, SDBD is a safe and clean biodiesel and a promising alternative biofuel.

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1 Introduction

Fossil fuels, mainly petroleum-based liquid fuels, natural gas and coal [1], remain to be a key factor in national economic development especially in developing countries like India and China. The transport sector is one of the fastest growing segments using fossil-based products in nowadays. Current transport system is based on combustion engines using fossil fuels, leading to greenhouse effect, reduction of biodiversity, desertification and many other ecological problems, which not only limit the nation's thriving but also threaten our own survival of humanity. Furthermore, for most industrialized countries there is a strong dependency on oil producing countries, which could cause political conflicts and even wars. Concerns about the depletion of fossil fuel reserves and the pollution caused by continuously increasing energy demands have stimulated the call for alternative fuels [2].

For the energy in electricity and heating power, there are sufficient alternatives available like photovoltaics, wind energy, and biomass. However, in the transport sector, the alternative energy is limited. Electric vehicles could be used in special segments of the transport sector like in urban areas, but due to the limited capacity of energy storage in batteries, these electrically powered cars could not substitute combustion engines in large extent within the next several decades. For aviation fuels, there has not been any suitable alternative to replace kerosene. The use of alternatively produced hydrogen basically could power combustion engines as well as electric cars with fuel cells, but because of the high price and lack of infrastructure there would not be a market penetration within the next decade. Currently, the only short-term alternative for the transport sector is the use of liquid biofuels [3], which are produced out from biomass and could be used in existing engines.

Global advanced biofuels development and production continues at a strong pace. Several European companies are producing cellulosic ethanol and renewable jet fuel at commercial scale. In Brazil, conventional sugarcane ethanol production is continuously expanded, both for domestic consumption and global export [4]. In 2012, Brazil exported 540 million gallons of sugarcane ethanol to the United States, and the export showed a continuously increasing trend since 2009 [5].

Biodiesel today is the most popular biofuel besides bioethanol. Biodiesel is a domestically produced, renewable fuel that can be manufactured from vegetable oils, animal fats, or recycled restaurant grease for use in diesel vehicles. Biodiesel's physical properties are similar to those of petroleum diesel, but it is nontoxic, biodegradable, and a cleaner-burning replacement for petroleum diesel fuel. Using biodiesel in place of petroleum diesel, especially in older vehicles, can significantly reduce emissions. Under the Energy Policy Act of 1992 (EPAct) and subsequent regulations [6], certain vehicle fleets operated by state agencies or alternative fuel providers are required to acquire alternative fuel vehicles. Covered fleets may also meet some of their requirements by using biodiesel blends of 20% (B20) or higher in medium- or heavy-duty vehicles. Figure 1 shows the amount of biodiesel purchased by covered fleets from 1999 to 2010.

Since the current situation of China is a large population verses a limited resources of arable land per capita, the selection of biodiesel feedstock should especially avoid competition with cooking oil. There is still much to be done to acquire feedstock from wild oil plants. There are approximately 300 million square kilometers of forest land throughout China, where oil plants cover 1554 species belonging to 697 genera and 151 families [7, 8]. A total of 38 oilseed crops have been identified as potential energy plants in China and are mainly distributed in tropical and subtropical areas. *Swida wilsoniana* is proposed as a candidate energy plant [9].
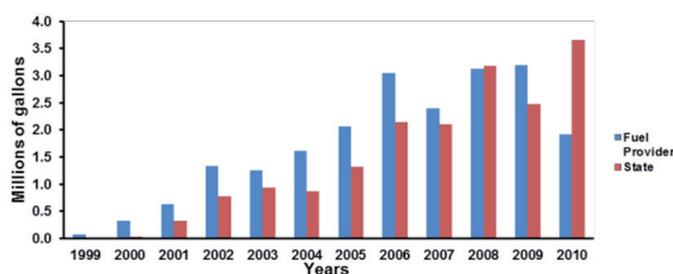
Fig. 1 Biodiesel purchased by covered fleets from 1999 to 2010
(Data Source: National Renewable Energy Laboratory EPAct Task,
http://www.afdc.energy.gov/afdc/data/)

Swida wilsoniana Wanger, a member of *Cornaceae*, is a woody oil plant with high-yield and high-oiliness characters in China [10]. It distributes in the forest land with an elevation ranging from 100 to 1000 m, an average temperature of 18-25 °C, and an annual precipitation of 1 000-1 570 mm. It can maintain maximum productivity for over 50 years and the life spans more than 200 years. An average of 50 kg dry fruits per year could be produced on a mature tree. Both fruit and seed have oil and the oil content in dry fruits is 33%─36% [11-13]. In this study, *Swida wilsoniana* fruit oil (SWO) was utilized for biodiesel production by transesterification and the reaction conditional parameters were optimized by orthogonal test.

2 Materials and methods
2.1 Materials
Fruits of Swida wilsoniana used for oil production in this study were collected in Longshan County, Hunan Province. All chemicals were purchased from Sigma Chemical Company (Saint Louis, Miss., U.S.A.). All solvents used were of analytical grade.

2.2 Preparation of refined SWO
Fruits of *Swida wilsoniana* were grinding firstly, and then raw oil was extracted by mechanical pressing. The raw SWO was degummed by hydrated method, decolored by clay, and deacidificated by alkali neutralization process. After those processes, the refined oil was dried in a drying oven.

2.3 Transesterification reaction mechanism
The transesterification reaction occurs in three consecutive and balanced stages, totaling six different rate constants. Triglyceride (TG) first reacts with methanol to produce diglyceride (DG), and then DG further reacts to produce monoglyceride (MG). Finally, MG reacts with alcohol to give glycerol (GL) as a byproduct, as following:

$$TG + ROH \leftrightarrow DG + RO_2R \qquad (1)$$

$$DG + ROH \leftrightarrow MG + RO_2R \qquad (2)$$

$$MG + ROH \leftrightarrow RO_2R + GL \qquad (3)$$

The overall reaction can be expressed as:

$$TG + 3ROH \leftrightarrow 3RO_2R + GL \qquad (4)$$

2.4 Orthogonal experimental design
The refined SWO was used for biodiesel production by transesterification. The main factors affecting the oil transesterification were molar ratio of methanol and oil (A), catalyst dosage (B), reaction temperature (C), and reaction time (D). To optimize the conditions, the SWO transesterification was carried out by an orthogonal experimental design of 4 factors and 3 levels [L_9 (3^4)] (Table 1).

Table 1 The orthogonal experimental design for SWO transesterification

Level	Independent variable			
	A (m:m)	B (wt%)	c (°C)	D (min)
1	5:1	0.9	40	60
2	6:1	1.0	60	90
3	7:1	1.1	80	120

2.5 Transesterification procedure

The SWO was added to the transesterification equipment and preheated to the desired temperature by agitation. After that, the catalyst was prepared by dissolving the sodium methoxide in the desired amount of methanol. This methanol solution was added to the SWO and the reaction was initiated at this time. The system was kept at room pressure and the experiments were carried out at constant temperature. The agitation as kept constant at 600 rpm to maintain uniformity of the mass transfer in the system. During the reaction time, samples were collected on an interval, diluted in tetrahydrofuran, cooled instantaneously and analyzed by the gas chromatography (GC) to evaluate the contents of TG, DG, MG,GL and ethylesters. The conversion ratio was obtained by analyzing the corresponding sample at 30 min of reaction with GC, which was calculated by dividing the peak area of the ester by the sum of the peak area of all components. After the reaction, the fuel mixture and the reaction products were cooled and placed overnight. Biodiesel and GL mixture were separated with a centrifuge, and then added the warm water into the mixture slowly. 10% H_3PO_4 was added into the mixture at a ratio of 1:300 (v/v) to remove the redundant methanol and the residual catalyst. Then, the mixture was stirring and statically separated. After repeating 3 times, the yield of biodiesel was calculated.

2.6 Physicochemical analysis

The raw biodiesel was redistilled under vacuum condition and the components purified biodiesel were analyzed by GC (Hewlett-packard model 5790A, USA). The conversion ratio can be calculated based on the results GC analysis. The kinematic viscosity of biodiesel was determined by an SYP1003-VI kinematic viscosimeter (Shanghai, China). The flash pointbiodiesel was determined by an SYP1003-III flashing point tester (Shanghai, China). Water Content in biodiesel was determined by an SYP1003-I moisture meter (Shanghai, China). The density of biodiesel was determined by an SYP1026 densimeter (Shanghai, China).

2.7 Data analysis

Data processing was carried out using SPSS 10.0 for Windows (IBM Corporation, Armonk, NY, USA).

3 Results and discussion
3.1 Relationship between conversion ratio and reaction time

In order to understand the relationship between the reaction time of transesterification and the ratio of conversion, the conversion ratio in the #4 run (Table 2) of the experiment were determined at intervals of each 20 min. It's apparently to see that a rapid increase of the conversion ratio at the first 60 min, a slow increase at 80-100 min, and then the reaction system was at a balance status after 100 min (Fig. 2).

The reaction speed was high at the beginning of reaction as the concentration of substrates was high and driving force was strong. The reaction speed then slowed down as the reaction went on due to the substrates consumption and products accumulation. The whole reaction system reached equilibrium when the positive force was balanced with the negative force. During this period, the conversion ratio was not increased with time, in verse, some negative reactions like saponification showed up with the passage of time, resulting in the reduction of biodiesel combustibility. Saponification occurs in alkali-catalysed homogeneous transesterification, depending on the hydroxide—alkoxide equilibrium [14].
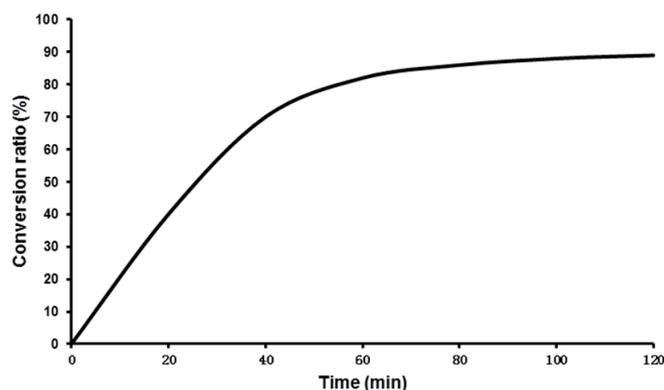
Fig. 2 Relationship between the reaction time of transesterification and the conversion ratio

Table 2 Results of L_9 (3^4) orthogonal test

Run	A	B	C	D	Conversion ratio (%)	Yield (%)
#1	1	1	1	1	86,23	82,13
#2	1	2	2	2	87,12	82,64
#3	1	3	3	3	95,12	88,56
#4	2	1	2	3	94,13	83,23
#5	2	2	3	1	88,23	86,45
#6	2	3	1	2	87,57	80,45
#7	3	1	3	2	80,13	75,23
#8	3	2	1	3	85,10	77,65
#9	3	3	2	1	88,40	79,86

3.2 Condition optimization

The results of orthogonal test for main factors affecting transesterification, i.e., methanol/oil molar ratio, catalyst dosage, reaction temperature, and reaction time, are showed in Table 2. The results of condition optimization for transesterification are summarized in Table 3. Table 3 shows the optimum condition for transesterification in biodiesel production from SWO is A1B3C2D3. When the methanol/oil molar ratio is 5:1, the conversation ratio of transesterification reached the maximum. Even more methanol was added, the reaction force would not be significantly enhanced. The transesterification is

usually a kind of nucleophilic substitution reaction (S_{N2}). The polarity of reaction system will increase with the concentration increase of methanol, which will slowly decrease the reaction rate as well as increase the cost of production. The conversion ratio increased with catalyst concentration, indicating that more catalyst promoted the transesterification of SWO. The conversion ratio was accelerated when the temperature increased from 40 to 60 °C. However, a decrease of the conversation ratio was observed when the temperature increased from 60 to 80 °C. This could be due to the increased rate of saponification with high temperature [15].

Table 3 Condition optimization for transesterifaction of SWO

Factor	Σ_1	Σ_2	Σ_3	F value	Optimum
A	295,47	269,93	269,93	1,331	A_1
B	260,49	260,45	269,93	0,615	B_3
C	258,90	269,65	269,93	0,476	C_2
D	262,86	254,82	269,93	1,577	D_3

3.3 Critical factor in transesterification of SWO

In arithmetic, the Range of a set of data is the difference between the largest and smallest values, which can be used to evaluate the impact extents of various variables. Result of Range comparison of four factors showed that the range of methanol/oil molar ratio was the biggest one, implying it was the most influential factor on the transesterification of SWO (Fig. 3). According the order of Range, the second factor was the reaction time, the 3rd one was reaction temperature, and the last one was catalyst dosage. Hence, the methanol/oil molar ratio was the critical factor and should be considered firstly when optimizing the conditional parameters.

Excess methanol in the reaction not only drives the transesterification equilibrium towards the product side and increases the rate of the reaction, but it also shifts the hydroxide‒methoxide equilibrium towards the formation of more methoxide ions, reducing saponification [14]. On the other hand, for the economic consideration, large amount of methanol to use can markedly increase the operational cost [16]. Therefore, a proper methanol/oil molar ratio is crucial for the biodiesel production.

3.4 Physicochemical characteristics of *Swida wilsoniana* biodiesel

The density, viscosity, cetane number, melting point, flash point and ash content of *Swida wilsoniana* biodiesel (SWBD) and 0# diesel were determined according to the standard methods [17] and the results are summarized in Table 4. It's easy to see that the characteristics of SWBD were similar to that of 0# diesel. However, SWBD has the advantages of high flash point (>105) and low ash content (<0.003). Therefore, SWBD is a safe and clean biodiesel and a promising alternative biofuel.
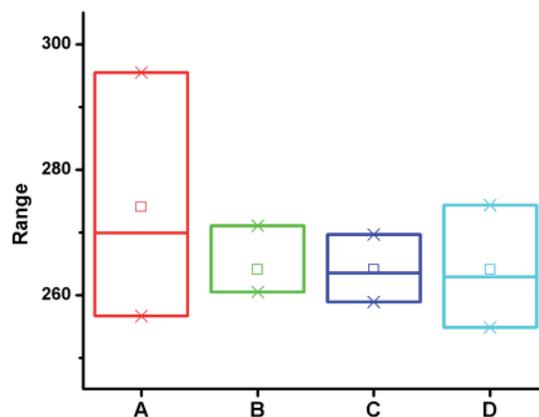
Fig. 3 Influential Range of various factors on conversion ratio

Table 4 Physicochemical characteristics of SWBD and 0# diesel

Material	Density (kg/L)	Viscosity (mm² s)	Catane number	Melting point (°C)	Flash point (°C)	Ash content
SWBD	0,891	5,60	38-41	-29,5	>105	<0,003
0#diesel	0,851	4,74	46	-7	>60	<0,025

4 Conclusions

Swida wilsoniana is a wild woody oil plant in China and widely distributed in the mountainous regions of calcareous sandstone. SWO could be conversed to biodiesel at a wide range of reaction conditions. The optimum conditions for transesterification of SWO were as follows: methanol/oil mole ratio 5:1, catalyst dosage 1.1%, reaction temperature 60°C, and reaction time 120 min. The characteristics of SWBD were similar to that of 0# diesel. It is a novel ideal alternative fuel with excellent mobility, safety and cleaning feature.

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