Preparation of Rich Hydrocarbon Fuels by Cornus Wisoniana Crude Oil Catalytic Coupling

Pengying Lai¹,², Jilie Li¹, Zhihong Xiao³ and Yifu Miu³, Aihua Zhang¹,²*

¹Central South University of Forestry and Technology, Changsha, Hunan, 410004, China
²Hunan Academy of Forestry, Changsha, Hunan, 410004, China
*Corresponding author’s e-mail: zhangaihua909@163.com

Abstract. Cornus wisonian is a woody energy plant unique to the southern region, the fruit oil can be used as the important raw materials in catalytic cracking. This experiment studied the catalytic cracking decarboxylation reaction of Cornus wisoniana oil. Through experiments, CaO / KF made by ourselves was proved to have good catalytic effect, gas production rate is lower than 12.0%, the by-product of the bottom of the kettle residue is controled under 5.0%, the yield of liquid fuel oil products is at 83.0% or more. Because of high acid value, pyrolysis oil can’t be directly burned. In this study, p-toluenesulfonic acid was used as a catalyst for alcohol esterification. Under the Optimization condition, acid value is lower than 1.0 mg KOH/g. Then alcohol esterification was used to reducing acid of cracking bio-fuel products and p-Methylbenzene sulfonic acid as catalyst. After reducing the acid, this kind of fuel is closer than traditional fossil fuels, able to alternative to diesel, and to achieve energy conservation.

1. Introduction
Cornus wisoniana is an important industrial oil energy tree species, mainly distributed in the south of the Yangtze River[1-4]. At present, the Cornus wisoniana oil is mainly converted into fatty acid methyl ester (biodiesel) by acid, alkali or enzyme catalyzed transesterification reaction of alcohol oil to prepare bioenergy. However, the production process of methyl ester biodiesel is complicated and its application range is limited[5]. Post-processing pollution emissions are difficult to solve and other issues restrict their further development.

The catalytic cracking process completely changes the physical and chemical properties from the molecular structure, and the obtained fuel oil has high calorific value, and the properties and composition are closer to the petrochemical oil[6-8]. The high-temperature cracking of the Cornus wisoniana oil to prepare the hydrocarbon-rich fuel is convenient and its requirements are simple. However, the bio-based hydrocarbon-rich fuel has a higher acid value, which reduces the stability of the fuel oil and even causes corrosion of the equipment, so it is necessary to carry out deacidification treatment[9]. In this study, the self-made refined Cornus wisoniana oil was used as raw material to study the catalytic cracking coupling esterification reaction process of woody oil, aiming to improve the quality of fuel oil. The effects of catalytic cracking parameters on the components of pyrolysis oil and the effects of catalytic esterification on the composition of pyrolysis fuel were investigated and the corresponding spectral analysis was carried out.
2. Materials and methods

2.1. Experimental materials and reagents
Methanol (AR, Tianjin Zhiyuan Chemical Reagent Co., Ltd.); Cornus wisoniana oil (hair oil, homemade); KF (AR, Shanghai Shanpu Chemical Co., Ltd.); KOH (AR, Beijing Tianfuda Industrial Co., Ltd.); p-toluenesulfonic acid (AR, Shanghai Feige Chemical Co., Ltd.); CaO (AR, Beijing Tianfuda Industrial Co., Ltd.)

2.2. Instrument
DF-101S magnetic stirrer; AUY-220 analytical balance; GC-2014 gas chromatograph; IS-5 FT-IR spectrometer; Scion SQ-bruker gas chromatography mass spectrometer.

2.3. Experiment method

2.3.1 Catalytic cracking method of Cornus wisoniana. The raw material light skin oil and the catalyst (the amount of the catalyst added is 1.5%) are introduced into a straight three-port glass reactor, stirred and uniformly mixed, and the reactor is assembled, and the electric furnace is directly preheated to 100 °C ~ 150 °C to remove residual moisture. The temperature is raised to 400 °C ~ 560 °C for the cracking reaction, and the product is a hydrocarbon-rich fuel.

2.3.2 Method for esterification of Cornus wisoniana oil cracking fuel. The Cornus wisoniana oil cracking product catalyzes the esterification reaction. The specific operation steps are as follows: 100 g of the catalytic cracking product is accurately weighed and transferred to a 250 mL three-necked flask at room temperature, and then p-toluenesulfonic acid is added as a catalyst in a flask, which will be called A good amount of methanol was transferred to a 250 mL constant pressure funnel. It is cooled by a serpentine condenser and heated in an oil bath. The temperature was raised to the experimentally required temperature, and the mixture was dropped into a flask in a constant pressure funnel, and the reflux state of the flow was observed to adjust the temperature. The water discharge in the water separator was observed to judge the degree of conversion of the reaction. Until the system has no moisture to stop heating, naturally cool to room temperature. Transfer to a separatory funnel to separate excess methanol and water, first wash with 5% NaCl salt, then add deionized water for 2~ 3 times to obtain an esterified oil.

2.3.3 Analysis of main components of Cornus wisoniana oil. The analysis of the fatty acid composition of the oil and fat was carried out by gas chromatography.

The chromatographic conditions were as follows: FFAP-quartz glass capillary column, column length 60 m, column diameter 0.3 mm; carrier gas N2: 81 kPa; carrier gas split ratio 100:1; H2 flow rate: 30 mL/min; air flow rate: 500 mL/min; Inlet temperature 260 °C; FID temperature 280 °C; set temperature range: 180 °C ~ 240 °C, heating rate: 6 °C / min.

3. Results and discussion

3.1. Analysis of the composition of raw material Cornus wisoniana
3. By gas chromatography analysis, it was found that the fatty acid above C16 was 96.12%, and the oleic acid was more than 42%. It can be speculated that Cornus wisoniana is a good industrial raw material for the preparation of hydrocarbon-rich fuel.

3.2. Catalytic cracking reaction of Cornus wisoniana oil

3.2.1. Effect of temperature on catalytic cracking reaction. Under the condition of reaction time 80 min and catalyst dosage 0.8% (raw material oil mass ratio), the effect of cracking temperature on the catalytic cracking reaction of Cornus wisoniana oil was investigated. The temperature range was from 400 °C to 560 °C.

It can be seen from Figure 2 that the optimum reaction temperature is 500 °C, and the product yield is the highest. Excessive reaction temperatures result in the production of more small molecular components, which are discharged as non-condensable gases, causing waste of resources; too low reaction temperatures lead to incomplete cracking.

3.2.2. Effect of CaO/KF content on catalytic cracking reaction. Under the condition of reaction time of 80 min and reaction temperature of 500 °C, the effect of the amount of catalyst on the catalytic cracking experiment of Cornus wisoniana oil was investigated. Investigate the range of catalyst dosage: 0.0%~1.6%.
When the content of CaO/KF is less than 1.2%, the amount of catalyst in the reaction system is insufficient, resulting in a decrease in reactivity, and the optimum reaction equilibrium is not achieved. The CaO/KF content of 1.2%~1.6% of the catalyst dosage stage results in low product yield due to the excessive number of active sites of the catalyst, and the excessive catalytic performance causes more small molecular components to be discharged, resulting in a reduction in effective products. When the CaO/KF content was 1.2%, the liquid phase yield reached a maximum of 82.11%. The optimum catalyst dosage is 1.2%.

3.2.3. Effect of Time on Catalytic Thermal Cracking reaction. Under the condition of reaction temperature of 500 °C and catalyst content of 1.2%, the influence of reaction time on the catalytic cracking experiment of Cornus wisoniana oil was investigated. The main time range was 30min~100min.

It can be seen from Fig. 3 that the reaction time of CaO/KF catalytic cracking is 80 min, and the product yield reaches 80% or more. The long or short reaction time will cause an increase in side reactions and even coking, resulting in product loss.

3.3. Product Mass Spectrometry
Reaction conditions: the catalyst KF/CaO content is 1.2%, the reaction time is 80 min, and the reaction temperature is 500 °C. Under this condition, the liquid phase cracking fuel yield is greater than 82%, and the temperament spectrum is as follows.
According to the gas mass spectrogram results in Fig. 5, the Cornus wisoniana oil cracking products mainly consist of the following components: saturated alkane (C8~C21) and olefin (C8~C21) compounds, and carboxylic acid compounds cycloalkane compounds and aldehyde compounds having corresponding carbon number distribution. Among them, olefin compounds, carboxylic acid compounds and aldehyde compounds are the main reasons for the instability of cracking products. The verification results of GC - MS chromatogram provide a basis for the necessity of subsequent post-esterification treatment.

3.4. Cleavage products catalyze esterification
Esterification conditions are as follows. The molar mass ratio of methanol to Cornus wisoniana pyrolysis oil is 9:1, using p-toluene sulfonic acid as catalyst, the amount of which is 4% of the mass of the crude oil, the catalytic esterification reaction is 5 h, and the reaction temperature is 85 °C.

| Indicators                  | Before esterification pyrolysis | After esterification pyrolysis | bio-diesel | 0# diesel |
|-----------------------------|---------------------------------|---------------------------------|------------|-----------|
| Density(20°C)(Kg/m³)        | 0.88                            | 0.85                            | 0.87       | 0.845     |
| Kinematic Viscosity(mm²/s)  | 4.46/40°C                       | 3.55/40°C                      | 4.49/20°C  | 3.52/20°C |
| Acid Value(mgKOH/g)         | 136.44                          | 0.86                            | 0.51       | 0.56      |
| Calorific value(KJ/g)       | 36.2                            | 39.2                            | 38.2       | 43.1      |

It can be seen from Table 1 that after esterification of the Cornus wisoniana cracking oil, the acid value is reduced by 99.36%, which indicates that the acid component in the cracked oil is significantly reduced after esterification. The density is also reduced by 0.8 from 0.82 and the kinematic viscosity is also decreased by 21.31%, which may be related to the complex reaction occurring inside the oil in the presence of catalyst after methanol addition, and also related to the physical dilution of methanol. The calorific value increased by 7.66%. The above indicates that the physicochemical properties of the cracked oil after the p-toluene sulfonylate is significantly improved. Comparing with biodiesel, it is found that the esterified Cornus wisoniana cracking oil is closer to traditional diesel fuel than biodiesel.

Infrared analysis before and after esterification of photocatalytic oil catalytic cracking products:
It can be seen from Fig. 6 that the infrared spectrum of the hydrocarbon-rich fuel catalyzed esterification is very different, mainly in the following bands: 2800 cm\(^{-1}\)~3200 cm\(^{-1}\), 1700 cm\(^{-1}\)~1800 cm\(^{-1}\), 1000 cm\(^{-1}\)~1200 cm\(^{-1}\). The specific analysis is as follows: 2800 cm\(^{-1}\)~3200 cm\(^{-1}\) represents the vibration of saturated CH. The catalytic reaction reacts the unsaturated part of the molecule to increase the saturated CH structure, so the peak shape of the hydrocarbon-rich fuel is deeper after the reaction; 1700 cm\(^{-1}\)~1760 cm\(^{-1}\) represents the ester carbonyl group. After esterification, the peak shape is sharper and stronger than before esterification, indicating that there are a large number of ester-based functional groups in the hydrocarbon-rich fuel after the reaction, which ensures the stability of the fuel; 1000 cm\(^{-1}\)~1200 cm\(^{-1}\) represents the absorption peak caused by the vibration of the CO bond in the ester. After the esterification, the hydrocarbon-rich fuel has a stronger peak in the wavenumber range, indicating that most of the carboxylic acid in the hydrocarbon-rich fuel after esterification. It has been converted to the corresponding ester.

4. Conclusion
In this experiment, the catalytic cracking reaction of the Cornus wisoniana oil was studied and analyzed, and the following conclusions were drawn.

The optimum conditions for the catalytic cracking of the Cornus wisoniana oil are as follows: the catalyst KF/CoO content is 1.2%, the reaction time is 80 min, and the reaction temperature is 500 °C. Under this condition, the liquid phase cracking fuel yield is greater than 82%; Pyrolysis fuel The finished fuel is obtained by esterification after high esterification. The molecular structure and physical and chemical properties are more similar to 0# diesel. It can replace some fossil energy by mixing to achieve energy saving and emission reduction.

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