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Research Paper

Production of mid-distillation fuels from syngas using cobalt nanocatalyst supported on Gracilaria gracilis macroalgae biochar

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1. ABSTRACT

This study investigates the application of biochar from the macroalgae pyrolysis of Gracylaria gracilis as catalyst support for producing mid-distillation fuels. Macroalgae were pyrolyzed at 550 °C, and the resulting products were evaluated. The major product of the pyrolysis was biochar (40.1%). The gaseous product mostly contained carbon dioxide (51.9%) and hydrogen (26.3%), and the liquid product mainly contained oxygenate and nitrogenate compounds. The biochar was activated and impregnated with 15% cobalt and then used as a catalyst in the Fisher-Tropsch process under syngas flow of 45 ml/min (H_2 / CO = 2), 18 bar pressure and temperature of 220 °C. 15wt.% Co/γ-Al_2O_3 as an industrial catalyst was used to compare performance in the Fischer-Tropsch process. The carbon monoxide conversion was 64.2% in the presence of the Co/Active Char catalyst and 58% for the Co/γ-Al_2O_3 catalyst. The results also showed that the Co/Active Char was more selective (74%) than the Co/γ-Al_2O_3 (70%) for highly valuable C^{5+} heavy hydrocarbons. In contrast, the selectivity of CH_4 and C_2-C_4 light hydrocarbon products for the Co/γ-Al_2O_3 catalyst was higher. Furthermore, the selectivity of carbon dioxide as a by-product was higher for Co/Active Char (2.3%) compared to Co/γ-Al_2O_3 (2%). Catalyst characterization was performed by BET, XRD, TPR, TGA and TEM methods.

Keywords: Pyrolysis; Gracilaria gracilis macroalgae; Biochar; Cobalt Catalyst; Fischer-Tropsch

2. INTRODUCTION

Fischer-Tropsch synthesis provides a green alternative for fuel production by converting syngas to hydrocarbon (Equation (1)). This method produces hydrocarbons from methane to long carbon chains such as gasoline and diesel.

$$CO + 2H_2 \leftrightarrow -(CH_2)- + H_2O \quad (1)$$

Cobalt-based catalysts (Co/SiO_2, Co/Activated Carbon, Co/Alumina, etc.) due to their high activity, high reaction stability, low cost, higher C^{5+} selectivity and less tendency for water gas-shift reaction has attracted more attention[1]. Common oxide supports used for the Fischer-Tropsch process include MgO, TiO_2, Al_2O_3 and SiO_2. The main problem of these supports is the interaction between the support and the metal, which leads to the formation of non-reducible mixed compounds. In contrast, due to weak interaction with metal precursors, carbonaceous supports have attracted a lot of attention to overcome this defect. Their high surface area causes high metal dispersion and as a result, forms small metal particles which improve the catalytic performance [1]. In the past years, biomass was significant as a cheap source for preparing activated carbon and using as catalyst support for various processes. Pyrolysis is one of the most advanced and efficient thermal conversion methods to convert biomass into carbon-rich solid compounds (biochar). In addition to this product, other high-energy

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products, including non-condensable gases (biogas) and condensable compounds (bio-oil), are also obtained, which can have special applications depending on their physical and chemical properties [2].
Few studies have been done on using algal biomass as support for Fischer-Tropsch synthesis catalysts. These algae change the ecosystem and have adverse effects on marine life. Therefore, in this study, the red Gracilaria gracilis macroalgae, which grows naturally on the Caspian Sea coast was used as feedstock for the pyrolysis process to produce bio-products, especially biochar. After activation with acid and the impregnation of 15% cobalt, the generated biochar was used as an effective catalyst in producing liquid hydrocarbon fuel from syngas during the Fischer-Tropsch process. The characteristics of the prepared macroalgae, the distribution of the pyrolysis products, the characteristics of the synthesized catalyst, as well as the activity and selectivity of this catalyst in the operating conditions of the Fischer-Tropsch process were extensively investigated.

3. MATERIALS AND METHODS

3.1. Pyrolysis experimental procedure

The pyrolysis was carried out under operating conditions of 550 °C, 30 min reaction time, 30 ml/min carrier gas flow rate and loading of 1 gr of algae in a quartz glass tube as a fixed bed reactor. The bioproducts included biochar, bio-oil and biogas. The feedstock was characterized by TGA, CHNS and biochemical analysis methods. Also, gas chromatography with a TCD detector and mass spectrometer was used to analyze the composition of gaseous and liquid products, respectively.

3.2. Catalyst preparation and Fischer-Tropsch experimental procedure

The biochar obtained in the pyrolysis process was activated by acid solution and carbonization. Then, 15wt. Cobalt was impregnated on the support surface. The synthesized catalysts were characterized by BET, XRD, TPR, TGA and TEM methods. Also, 15wt.% Co/γ-Al_2O_3 as an industrial catalyst was used to compare performance in the Fischer-Tropsch process. These catalysts were used under conditions of syngas flow of 45 ml/min (H_2 / CO = 2), 18 bar pressure, a temperature of 220 °C and catalyst loading of 1.5 grams. Before starting the process, the catalyst was regenerated under hydrogen flow (50 ml/min) at 400°C for 14 hours.

4. RESULTS AND DISCUSSION

4.1. Pyrolysis process

The yields of the bioproducts and gaseous product composition generated from the pyrolysis of the macroalgae are shown in table 1. According to table 1, the highest yield was for biochar (40.1%), which can be attributed to the high content of fixed carbon and ash in its structure. Also, the gas composition shows that the highest efficiency is related to carbon dioxide (51.9%) and hydrogen (26.3%).

Table 1. Bioproduct yields and biogas composition of macroalgae pyrolysis at 500 °C

Yield (wt.%)			Biogas composition (V/V.%)				
Biogas	Biochar	Bio-oil	CO_2	CO	H_2	CH_4	C_2-C_4
20.9	40.1	39.0	51.9	14.5	26.3	5.4	1.9

According to GC/MS data, bio-oil was a complex combination of organic substances which can be classified into nine categories: hydrocarbon (12%), phenol (11.4%), alcohol (11%), acid (14.1%), ketone (12%), ester (12%), furfural (9.5%), nitrogen-containing compound (6.9%), and compounds containing nitrogen-oxygen (7.6%). Depending on the compounds present, bio-oil can be used in many applications such as electricity and heat generation, transportation fuel and chemicals. Due to high amounts of acids and ketones, bio-oil can be unstable and corrosive during transportation and storage.

4.2. Catalyst performance in Fischer-Tropsch process

The performance of Co/Active Char and Co/γ-Al_2O_3 catalysts for Fischer-Tropsch synthesis are shown in Table 2. The CO conversion was 64.2% for Co/Active Char and 58% for Co/γ-Al_2O_3. The activity of the catalyst depends on reduction of active metals on the support surfaces. Investigating the performance results of the catalyst also showed that the Co/Active Char was more selective than the Co/γ-Al_2O_3 for highly valuable C^{5+} heavy hydrocarbons (74%). The activity of the synthesized catalyst in the reactor test has led to the formation of CO_2, which is known as a side product and is attributed to the water-gas shift reaction. The results showed that the CO_2 production was higher for the Co/Active Char catalyst because of its higher activity. Also, comparing its performance with other expensive carbon-based industrial catalysts such as carbon nanotubes and graphene showed that the carbon monoxide conversion was higher and the selectivity of heavy compounds was close to them. Therefore, it can be used as a cheap and effective alternative catalyst in this industry.

Table 1. Comparing the performance of Co/Active Char catalyst in the Fischer-Tropsch process with other industrial catalysts

Catalyst	Operating conditions			CO Conversion (%)	Selectivity				Ref.
	Temp. (°C)	Pressure (bar)	H_2/CO		CH_4%	CO_2%	C_2-C_4%	C_5^+%	
15Co/Active Char	220	18	2	64.2	9.3	2.3	12.1	74	This Study
15Co/γ-Al_2O_3	220	18	2	58	12.5	2	13	70	This Study
15Co/AC	220	30	2	30.2	24	2.1	22.5	32.8	[3]
15Co/CNT	220	25	2	45	11	-	-	83	[4]
15Co/Graphene	220	18	2	60	10.2	1.3	1.4	87.1	[5]

5. CONCLUSION

In this research, cobalt nanocatalyst supported on biochar obtained from the pyrolysis of red macroalgae Gracilaria gracilis was used to produce mid-distillation fuels in the Fischer-Tropsch process. The results showed a high conversion for carbon monoxide and high selectivity of heavy hydrocarbons compared to methane and light hydrocarbons, and overall, it has been a better performance compared with alumina and other expensive carbonaceous-supported industrial catalysts.

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