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Gasification of sunflower seed pulp for the synthesis of hydrogen-rich products

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Abstract

Gasification of biomass has great potential for satisfying the ever-growing demand for a clean and renewable energy source. In this study, sunflower seed pulp, a waste product of sunflower oil factories, was gasified using K_2CO_3 as a catalyst and dry air as a gasifying agent. Effects of reaction temperature, dry air flow rate and catalyst ratio on the gas product composition were investigated. The highest hydrogen yield (5.45 mol/kg biomass) was achieved at 750 °C, with the addition of 20 wt.% K_2CO_3 and with a dry air flow rate of 3 L/h.

Keywords: Gasification, hydrogen, sunflower seed pulp, sunflower meal

1. Introduction

Worlds energy demand is being satisfied mostly with petroleum fuels, coal and natural gas. It has been realized that those sources are unsustainable and have harmful effects on the environment. Therefore, the search for cleaner and more reliable, renewable energy sources has gained a lot more importance recently [1]. Hydrogen is a promising, clean and renewable power source. Three main methods of producing hydrogen-rich gas are pyrolysis, catalytic steam reforming and gasification [2].

Hydrogen is mainly produced through natural gas reforming, which is a costly process [3]. According to market research in 2018, high purity hydrogen costs approx. 8 \$/kg H_2 which equates to 66.4 \$/GJ energy produced.

This study aims to reduce the cost of hydrogen production through the gasification of sunflower seed pulp (sunflower meal/sunflower oil cake), which is a waste biomass of sunflower oil factories. Most of the leftover pulp after oil extraction is being used as fodder or fuel without any treatment [4].

The gasification method yields gaseous products with higher hydrogen to carbon ratio than other methods like pyrolysis. The hydrogen-rich gases produced from the biomass can be purified or combusted on-site to produce electricity for powering sunflower oil factories.

There is limited research in the literature about the gasification of sunflower seed pulp. According to the 2013 data, the annual sunflower seed production rate of Turkey is 1 380 000 tons. Zabaniotou et al. have performed pyrolysis of sunflower seed pulp at 300-600 °C, 1 atm, under helium atmosphere. They reported that the highest gas yield (53% wt. gas/wt. biomass) was obtained with a gas flow rate of 50 cm^3/min, a heating rate of 40 °C/s and a reaction temperature of 500 °C [5].

Christodoulou et al. gasified sunflower seed pulp using a continuous fluidized bed reactor. Highest hydrogen composition (28.6 vol.%) was achieved at 800 °C, 1 atm. Biomass and air feed rates, and total gas product flow rates were 6.8 kg/h, 7.8 m^3/h, and 15.61 m^3/h, respectively, which is approximately equal to 7.46 mol H_2/kg biomass [6].

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Shie et al. investigated the effect of K_2CO_3 on the pyrolysis of sunflower seed pulp using a 60 kW pilot-scale plasma torch reactor at 1 atm, 700°C, and with an N_2 flow rate of 100 L/min. It was determined that the addition of 20 wt.% K_2CO_3 yields to H_2, CO and CH_4 concentrations of 44.31, 42.91 and 12.76 vol.%, respectively [7].

In the literature, reported values of lignin and hemicellulose content of sunflower seed pulp vary between 6.1%-26.8% and 12.6%-33.3% respectively. No data regarding the benzene-ethanol extractive content of this particular biomass was found. However, the extractive content of the sunflower seed hulls varies between 0%-5.3% [8–11].

2. Materials and Methods

2.1. Material

Sunflower seed pulp was obtained from an oil factory located in western Turkey. High purity K_2CO_3 and dry air were used in the experiments.

2.2. Equipment

An updraft gasifier was used for the gasification of biomass. The gasifier is a 900 mm long, 316 stainless steel tube with an internal diameter of 10 mm. An external power supply allows the reactor to heat up to 850 °C in 60 seconds. The reactor has a removable ceramic outer shell for heat insulation.

Products are separated by a liquid-gas separator. The gaseous product goes through the moisture and particle filters before the gas sampling bag. The dry air flow rate is regulated by a standard flow meter (Fig. 1).

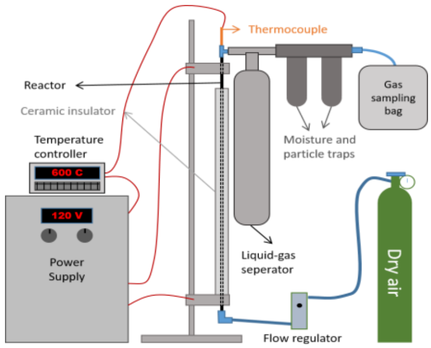

Fig. 1. Experimental setup.

Analysis of the product-gas was done using an SRA Technologies Micro Gas Chromatograph (μ-GC) (T-3000 series) equipped with MS5A (Molecular sieves 5 Å) and PPQ (PolarPlot Q) columns coupled to thermal conductivity detectors (TCD). A standard gas mixture was used to calibrate the μ-GC. Helium and argon were used as carrier gases.

2.3. Experimental procedure

Prior to any experiment, air dried biomass was milled in a rotary cutter mill at 8000 RPM and then dried at 105 °C for 24h.

2.3.1. Proximate analysis

Proximate analysis was performed on the biomass using standard methods [12,13]. According to the analysis results, it contains 4.47% moisture, 1.48% extractives, 69% hemicellulose and 18.5% lignin.

2.3.2. Gasification of sunflower seed pulp

The biomass was gasified using an updraft gasifier. Experiments were conducted at different temperatures (650, 750 and 850 °C), catalyst to biomass ratios (0, 20 and 40% wt./wt.) and dry air flow rates (1, 2, 3 and 4 L/h) to determine suitable reaction parameters.

For each experiment, 3 g of biomass was mixed with the catalyst (K_2CO_3) at desired ratios and placed into the reactor between two layers of wire mesh filter as a fixed bed. Then, the reactor was inserted into the ceramic insulator shell. After that, the liquid/gas separator and the dry air inlet pipe were connected to the reactor. The reactor temperature was adjusted with a temperature controller unit. After the setup procedure, the external power source was switched on to start the reaction. The temperature controller was set to reach the desired temperature in three minutes. Experiments were carried out at a constant reaction time of 15 minutes and 1 atm. Gaseous products were collected in the gas sampling bag and then introduced into the μ-GC in order to find out the gas composition.

3. Results and Discussion

The effects of reaction temperature, dry air flow rate, and catalyst ratio on the product-gas yield were determined. Component yields of carbon monoxide (CO), carbon dioxide (CO_2) and hydrogen (H_2) in the product-gases of each experiment were determined. The total yield of methane (CH_4), ethane (C_2H_6), ethylene (C_2H_4), propylene (C_3H_6) and propane (C_3H_8) were also determined and reported as C_nH_n.

3.1. Effect of reaction temperature

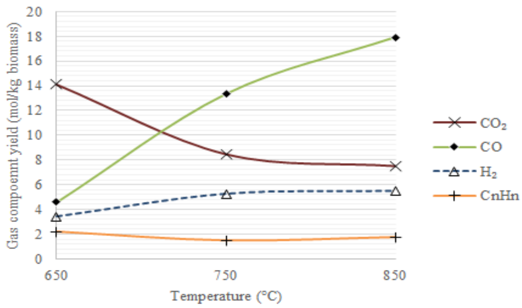

Fig. 2. Effect of temperature on gas yields @ 3 L/h dry air input rate, without any catalyst.

According to Fig. 2, hydrogen yield increases with temperature by approx. 60%. A similar increase can be observed in carbon monoxide, which almost quadruples. He et al. found similar results and it was explained by Le Chatelier's principle [14].

The highest hydrogen (5.49 mol/kg biomass), methane (1.43 mol/kg biomass) and carbon monoxide (17.92 mol/kg biomass) yields, as well as the lowest carbon dioxide (7.48 mol/kg biomass), ethane (0.14 mol/kg biomass), ethylene (0.078 mol/kg biomass), propylene and propane (both around 0.05 mol/kg biomass) yields were achieved at 850 ℃.

3.2. Effect of dry air flow rate

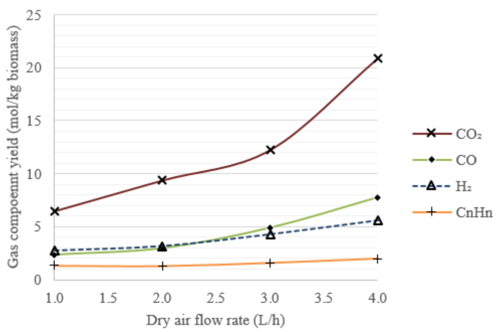

Fig. 3. Effect of dry air feed rate on gas yields @ 20 wt.% K_2CO_3, 650 ℃.

Fig. 3 illustrates that hydrogen yield increases steadily with the dry air flow rate since the stoichiometry of the reactions that favor the hydrogen production are satisfied adequately. The molar composition of hydrogen decreases by 3% and 20% at the flowrates of 3 L/h and 4 L/h respectively because of the inert nitrogen gas in the dry air mixture. Having a diluted product-gas could potentially increase the cost of purification; therefore the suitable flowrate was determined as 3 L/h. At this condition, hydrogen, methane and carbon monoxide yields increase by 57%, 45% and 168% respectively.

The highest hydrogen (5.63 mol/kg biomass), carbon monoxide (7.75 mol/kg biomass), carbon dioxide (20.87 mol/ kg biomass), methane (1.072 mol/ kg biomass), ethane (0.37 mol/ kg biomass), propane (0.15 mol/ kg biomass) and propylene (0.17 mol/ kg biomass) yields were obtained using a dry air flow rate of 4 L/h with the lowest ethylene yield of 0.19 mol/ kg biomass.

3.3. Effect of catalyst to biomass ratio

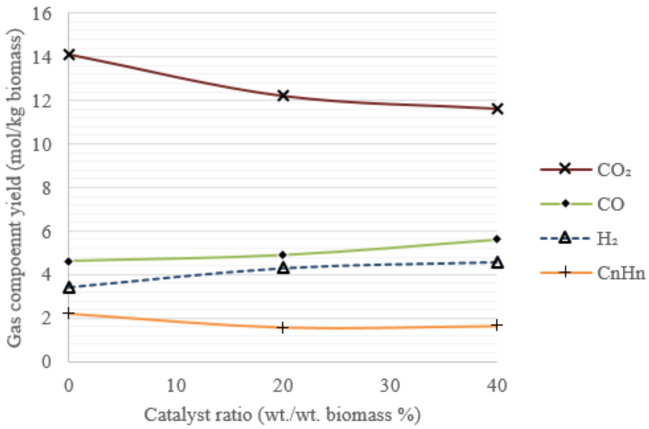

Fig. 4. Effect of K_2CO_3 to biomass ratio on gas yields @ 650 ℃, 3 L/h dry air flow rate.

Fig. 4 shows that hydrogen and carbon monoxide yields increase with the catalyst ratio up to 4.59 and 5.63 mol/kg, respectively. The yields of ethylene, ethane, propylene, and propane, as well as carbon dioxide decrease with higher catalyst ratios. Demirbas reported that the use of K_2CO_3 can prevent the formation of stable chemical structures in the products and weaken the C–C bond by an oxygen transfer mechanism, thus decreasing the activation energy of the complex pyrolysis reaction [15]. This phenomenon might be the cause of the decrease in C_{2+n} components.

The increase in hydrogen yield between the catalyst ratios of 20% and 40% is only 6%; therefore it might be more economical to use a catalyst ratio of 20%.

When 20% catalyst ratio was used at 750 and 850 °C, the hydrogen yields were observed to be 5.48 and 7.11 mol/kg biomass, respectively. These findings are similar to what Christodoulou et al. reported (7.41 mol/kg at 850 °C) under the same conditions[6]. The slight surplus in their hydrogen yield is most probably caused by their use of a continuous reactor, instead of a batch reactor.

4. Conclusion

In this research utilization of sunflower seed pulp was investigated in order to obtain hydrogen-rich gaseous products. Effect of gasification reaction parameters such as temperature (650, 750, 850 °C), airflow rate (1, 2, 3, 4 L/h) and catalyst ratio (0, 10, 20, 30, 40%) on the hydrogen yield was examined.

The hydrogen yield of the studies carried out without catalyst at 850 °C and with 20% K_2CO_3 catalyst at 750 °C were found to be 5.49 and 5.45 mol/kg biomass, respectively. Since these values are almost the same, the appropriate operating condition was determined as 750 ^oC using 20% K_2CO_3 and air flow rate of 3 L/h.

Acknowledgment

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