HYDROGEN-RICH GAS PRODUCTION VIA TWO-STEP GASIFICATION OF SUNFLOWER MEAL

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Abstract - Sunflower meal was liquefacted at different temperatures, reaction times, water:biomass ratios, and catalyst:biomass ratios. Highest hydrogen yield (5.55 mol H_2/kg sunflower meal) was obtained at 350 °C, 60 min, using a catalyst ratio of 10 wt.% and water:biomass ratio of 50:1 (wt.:wt.). Liquid product of this reaction (contains 74 mol% acetyl tributyl citrate) was gasified through catalytic steam reforming in a continuous reactor at different temperatures and water:liquid ratios. Highest hydrogen yield (9.30 mol H_2/kg liquid) was achieved at 800 °C and 24:3 water:liquid ratio (vol.:vol.).

Keywords - Sunflower meal, liquefaction, gasification, hydrogen

I. INTRODUCTION

Main sources of energy are petroleum fuels, coal and natural gas which are known to be unsustainable and hazardous to the environment [1]. Liquefaction and gasification products of various biomass could replace these sources with reliable and clean alternatives. One of the products of biomass conversion is hydrogen, which is a clean and promising energy carrier. Main methods of hydrogen-rich gas production are pyrolysis, catalytic steam reforming and gasification [2].

Sunflower meal (SFM) is a waste biomass of sunflower oil factories. Its main uses are as fodder or fuel. According to the 2013 data, the annual sunflower seed production rate of Turkey is 1,380,000 tons [3].
Christodoulou et al. gasified SFM using a continuous fluidized bed reactor. Highest hydrogen composition (28.6 vol.%) was achieved at 800 °C, 1 atm. Biomass and air feedrates and gas output rates were 7.8 m^3/h, 15.61 m^3/h and 15.61 m^3/h, respectively [4].

Zabaniotou et al. pyrolyzed SFM at 300-600 °C, 1 atm using a helium atmosphere. Highest gas yield (0.53 wt./wt. SFM) was obtained at 500 °C, with a heating rate of 40 °C/s [5].

Hasanoglu et al. liquified woody kenaf biomass in an aqueous environment, at 250-325 °C, for an hour, using different water to biomass ratios, with a high-pressure (7-270 bar) batch reactor. Highest gas volume (352 mL) and hydrogen composition (39 mol%) were achieved at 250 °C when 5 wt.% RuC and 6:1 water:biomass (wt.:wt.) ratio was used [6].

Muangrat et al. investigated the gasification of various food products in an alkaline aqueous environment. NaOH aided the decomposition of every biomass they used, decreased the tar formation and increased the hydrogen yield by promoting the water-gas shift reactions [7].

Nanda et al. gasified pinewood with a tubular batch reactor at different temperatures, water:biomass ratios, and reaction times. Highest hydrogen yield (5.8 mol H_2/kg biomass) was achieved at 500 °C, 45 min, 230 bar, using biomass impregnated with Nickel and a water:biomass ratio of 10:1 (wt.:wt.) [8].

Posmanik et al. liquefied a model mixture of sugar, proteins and lipids in a high-pressure batch reactor. Highest liquid yield (67 wt.%) was achieved using KOH and a water:biomass ratio of 50:1, at 20 bar, 300 °C and 60 minutes [9].
Kim et al. liquefied sunflower stalk in a batch reactor, using glycerol and sulfuric acid. Highest liquid yield (59 wt.%) was achieved using a glycerol:biomass ratio of 10:1 (wt.:wt.), 4 wt.% sulfuric acid, at 150 °C, 1 bar and 60 minutes [10].

Irmak et al. liquefied kenaf biomass using high-pressure (276 bar) batch reactor, with a water:biomass ratio of 46:1 (wt.:wt.), under a CO_2 atmosphere, for 90 minutes, at 250 °C. Later on, they gasified the liquid product of this experiment in a micro-bench batch reactor at 250 °C, using 2 wt.% Pt:C catalyst for 2 hours. Highest hydrogen composition (60 mol%) was achieved using the kenaf biomass liquefied at 250 °C [11].

There is limited research about the gasification of SFM. Gaseous product that occurs during the liquefaction of SFM was mostly ignored in the literature.

In a previous study of the authors, sunflower meal (SFM) was gasified in a tubular batch reactor. The highest hydrogen yield (5.45 mol H_2/kg SFM) was obtained at 750 °C, with the addition of 20 wt.% K_2CO_3 and with a dry air flow rate of 50 mL/min [12]. In this study in order to improve hydrogen yield, a

two-step gasification method was used. SFM was liquefied in a batch reactor and the liquid product was gasified through catalytic steam reforming in a continuous reactor. Gas component yields were investigated and compared to the previous study.

II. MATERIAL AND METHODS

A. Material

Sunflower meal used in this study was acquired from a sunflower oil factory, located in western Turkey. Proximate analysis results of SFM were reported in a previous study as 4.47% moisture, 1.48% extractives, 69% hemicellulose and 18.5% lignin [12]. Before each experiment, SFM was ground in a rotary cutter mill at 8000RPM and dried at 105 °C for 24h.

Ready-to-use 30% Ni/Al_2O_3 catalyst used in the gasification experiments was previously synthesized and characterized [13].

B. Liquefaction

A 500 mL stirred Parr Model 4576 high-pressure batch reactor was used for the liquefaction process. The reactor is capable of reaching 350 °C in 45 minutes. Experiments were carried out at 90-120 bar pressure, under an inert nitrogen atmosphere, at varying temperatures (200, 300, 350 °C), reaction times (15, 30, 60 min), water to SFM ratios (10:1, 20:1, 50:1 wt.:wt.) and NaOH to SFM ratios (0, 10, 20, 30 wt.%). 2 g of SFM, desired amount of NaOH and water were added into the reactor. Then, the lid of the reactor was closed and the air left inside the reactor was purged using nitrogen for 5 minutes.

Finally, the reactor chamber was placed into the heater and the temperature controller was activated. After the reactor reached the desired reaction temperature, the reaction was carried out for 15 to 60 minutes, depending on the predetermined reaction time. Then, the heater and stirrer were turned off, the reactor chamber was removed from the heater and placed into an ice bath for rapid cooling. When the temperature dropped below 95 °C, cold water was sent through the reactor's coolant injection port, to increase the cooling speed.

After the temperature dropped to 20 °C, a water-cooled liquid-gas separator was attached to the gas outlet port of the reactor, and the gaseous products were collected in a gas sampling bag. When the gas collection was over, the liquid-gas separator and the lid of the reactor were removed, and the liquid-solid mixture was collected. The reactor was washed with dichloromethane (DCM) to recover any leftover DCM-soluble products, and this solution was added to the aforementioned liquid-solid mixture. The solid product was separated by vacuum filtration and oven-dried. The liquid product was separated into DCM-Soluble and water-soluble phases using a separating funnel. Elemental analysis was performed to the DCM-soluble liquid phase, and the solid product. GC-MS analysis was done to the DCM-Soluble phase. Gas composition was determined using a micro gas chromatograph (μ-GC).

C. Gasification

The most suitable liquid product acquired from the liquefaction experiments (LP) was gasified in a 45 cm long stainless steel tubular reactor. The reactor has an internal diameter of 0.8 mm and an outer diameter of 1.2 mm. Experiments were carried out at 1.5-2 bar pressure, varying temperatures (600, 700, 800 °C) and water to LP ratios (3:3, 8:3, 16:3, 24:3 vol.:vol.). The reaction system consists of 2 peristaltic pumps (PUMP1-2), 3 heated lines (HL1-3) that operate at 200 °C, 2 water cooled liquid-gas separators (SEP1-2) and 2 filters (FILTER1-2). The filters consist of glass fiber and silica gel, to capture solids and moisture (Fig. 1).

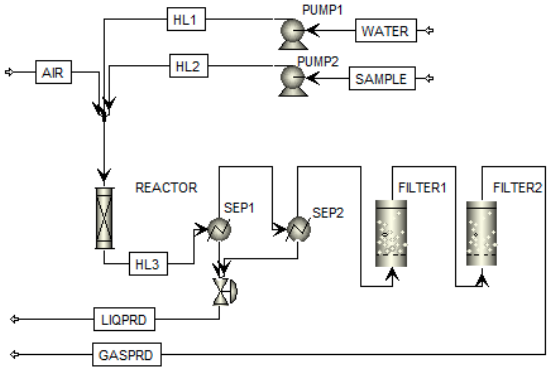


Fig 1. Flowsheet of the gasifier setup

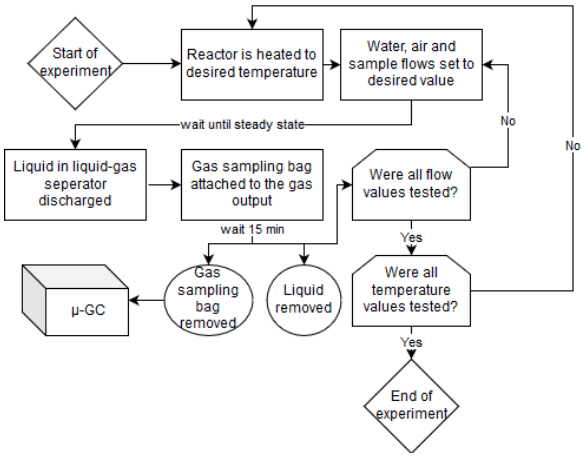


Fig 2. Flow chart of the gasification experiment

For each experiment, a dry air flow rate of 100 mL/min, and an LP feed rate of 0.12 mL/min was used. For catalytic runs, 0.5 g of Ni/Al_2O_3 was mixed with 2 mL of silicon carbide, and loaded into the reactor. The catalyst bed is held in place by two layers of quartz fiber to form a fixed bed. Flow chart of the experimental procedure is given in Fig 2.

D. Gaseous Product Analysis

Gas analysis was performed using an SRA Instruments Micro Gas Chromatograph (μ-GC)

(T-3000 series) equipped with MS5A (Molecular sieves 5 Å) and PPQ (PolarPlot Q) columns coupled to thermal conductivity detector (TCD). A standard gas mixture was used to calibrate the μ-GC. Argon and helium were used as carrier gases.

III. RESULTS AND DISCUSSION

A. Elemental Analysis

Elemental analysis of the SFM, solid and liquid products was done and the empirical formula of SFM was determined according to the analysis result as $(CH_{1,55}N_{0,16}O_{0,65})_n$.

B. Liquefaction Results

Table I illustrates gas compositions and product (solid, liquid and gas) yield according to different reaction parameters applied. When the reaction time is considered, there is no big difference in hydrogen content obtained at 30 and 60 minutes 1.38 and 1.29, respectively. Wherein the total gas product fraction increases significantly at 60 minutes reaction time therefore, following experiments were carried out at 60 minutes.

The highest hydrogen yield and total gas volume (1750 mL) was obtained with a water:SFM ratio of 50:1 (wt.:wt.), therefore 50:1 was determined to be the best ratio. The hydrogen yield at 350 °C is 330% higher than the hydrogen yield at 300 °C, wherein the total gas product fraction is only 9.56% lower, therefore 350 °C was selected to be the most suitable temperature.

On non-catalytic runs, almost no hydrogen was obtained, and tar formation was high. It was observed that the addition of NaOH mitigated these problems. These results are in accordance with Muangrat's report [7].

The reaction performed at 350 °C, 60 min, using a catalyst ratio of 10 wt.% and a water:SFM ratio of 50:1 (wt.:wt.) was selected as the most suitable one, therefore GC-MS and elemental analysis were performed on its products. 0.41 wt.% of the LP (liquid product) was DCM-soluble, and its empirical formula was found to be $(CH_{1,97}N_{0,08}O_{0,14})_n$ through elemental analysis. The empirical formula of the solid product is $(CH_{0,8}N_{0,02}O_{0,68})_n$. According to found results, an elemental mass balance calculation was made to determine the contents of the water-containing phase. According to the calculations, this phase contains 0.002 mol% C, 0.07 mol% N, 66.9 mol% H and 33.0 mol% O. Since the carbon and nitrogen content of this phase is negligible, its empirical formula can be assumed to be H_2O. This result proves that the liquid phase separated from DCM-soluble phase consists of only water.

GC-MS results of the DCM-soluble phase show that it contains 73.9 mol% acetyl tributyl citrate ($C_{20}H_{34}O_8$), 5.7 mol% decanoic acid ($C_{10}H_{20}O_2$) and various similar compounds.

C. Gasification Results

The results of non-catalytic gasification experiments at 800 °C are given in Fig. 3. When water:LP ratio is increased from 3:3 to 16:3 (vol.:vol.); hydrogen, carbon dioxide and hydrocarbon yields increase by 16%, 221% and 17% respectively whereas the carbon monoxide yield decreases by 20%. The highest hydrogen yield (1.58 mol H_2/kg LP) was obtained at 16:3 water:LP ratio. Total gas and liquid output rates were 175 and 0.84 mL/min, respectively.

Reaction Parameter		Gas component yields (mol component/kg SFM)				Product Yield (wt.%)		
		H_2	CO_2	CO	C_nH_m	Solid	Liquid	Gas *
Reaction time (min) [a]	15	0.49	3.38	17.01	0.08	0.23	**93.55**	6.23
	30	**1.38**	3.02	17.45	0.21	0.23	92.27	7.49
	60	1.29	3.51	19.00	0.22	0.24	83.75	**16.01**
Water:SFM ratio (wt.:wt.) [b]	10:1	0.72	2.15	14.22	0.26	1.93	62.19	**35.88**
	20:1	0.91	1.48	15.68	0.06	0.71	79.50	19.78
	50:1	**1.29**	3.51	19.00	0.22	0.24	**83.75**	16.01
Reaction temperature (°C) [c]	200	0.04	0.23	9.18	0.03	0.65	78.51	**20.84**
	300	1.29	3.51	19.00	0.22	0.24	83.75	16.01
	350	**5.55**	1.78	23.01	1.03	0.15	**85.37**	14.48
Catalyst ratio (wt.%) [d]	0	0.32	0.81	5.25	0.08	0.25	**91.56**	8.19
	10	1.29	3.51	19.00	0.22	0.24	83.75	16.01
	20	**2.74**	1.28	19.72	0.26	0.37	68.71	**30.91**

(a) @50:1 water:SFM, 300 °C, 10 wt.% NaOH **(b)** @60 min, 300 °C, 10 wt.% NaOH **(c)** @50:1 water:SFM, 60 min, 10 wt.% NaOH
(d) @60 min, 300 °C, 50:1 water:SFM * Calculated through mass balance

TABLE I. LIQUEFACTION RESULTS

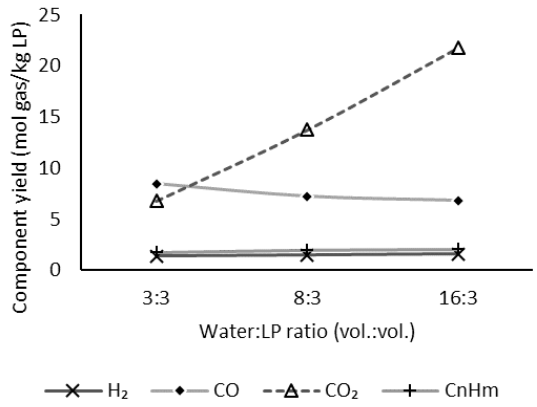


Fig.3. Noncatalytic gasification results (@800 °C, 100 mL Air/min, 0.12 mL LP/min)

According to Fig. 4 and 5 when either temperature or water:LP ratios are increased; hydrogen and carbon monoxide yields increase, while carbon dioxide and hydrocarbon yields decrease. Franco et al. explain that increasing temperature or water feed rate promotes water gas shift reactions, especially at temperatures higher than 700 °C [14]. Highest hydrogen yield (9.30 mol H_2/kg LP) was obtained at 800 °C and 24:3 water:LP ratio (vol.:vol.). Total gas and liquid output rates were 268 and 0.91 mL/min. At this condition, increasing water:LP ratio from 3:3 to 24:3 increased hydrogen and carbon monoxide yield by 234% and 729% while reducing carbon dioxide and hydrocarbon yields by 49% and 89%. When the results of the catalytic and non-catalytic runs are compared, it can be said that the presence of Ni/Al_2O_3 increases the hydrogen yield by 366%, and total gas output rate by 96%. The most notable fact is the change in CO and CO_2's trends. The catalyst lowers the CO_2 emissions and increases the CO yield. This effect is similar to what Kousi et al. observed [15]. This effect, combined with the increased hydrogen yield, increases the heating value of the gas product.

IV. CONCLUSION

In this study, the highest total hydrogen yield of the two-step gasification was found to be 14.85 mol H_2/kg SFM. In the previous gasification study of the authors of this paper, the highest hydrogen yield was 5.45 mol H_2/kg SFM. The two-step gasification process used in this work improved this value by 172.47%.

The conditions in which the highest hydrogen yields and gas fractions were achieved are similar to the ones reported in the literature [4][7][9].

Nanda et al. and Christodolou et al. both gasified solid biomasses without liquifying them first, and the highest hydrogen yields they achieved are 5.80 and approx. 7.62 mol H_2/kg, respectively. When the combined results of this study are compared to theirs, the total hydrogen yield achieved in this work is higher, due to the effect of liquefaction [4][8].

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