

Hydrogen production through gasification of whey

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Abstract. Hydrogen is one of the clean energy carriers and it is obtained from fossil and renewable energy sources and waste of the food industry. In this study, whey, which is the waste of the cheese factory, was gasified using a high-pressure batch reactor at different temperatures (300, 350, 400 °C) and an updraft tubular reactor at (650, 700°C). In order to find out suitable gasification conditions, the effect of reaction parameters such as catalyst type (K₂CO₃ and NaOH), temperature (300-700 °C) and time (30-120 min) were investigated. The highest hydrogen yield (14.47 mol H₂/kg Whey Powder-2) was obtained with 2.51 M NaOH at 120 min. reaction time at 400 °C.

1 Introduction

The energy demand has been increasing with the developing industry. Conventional energy sources, such as coal, petroleum and natural gas are limited and hazardous to the environment. Biomass is a clean alternative energy source that can be used to mitigate environmental pollution through the reduction of greenhouse gas emissions [1]. Production of hydrogen from biomass is divided into two groups as thermochemical (i.e. pyrolysis, gasification, and liquefaction) and biological (i.e. biophotolysis and fermentation) processes [2]. Gasification is one of the thermochemical processes that convert feedstocks into useful gases and chemicals in the presence of a gasification agent (air, oxygen, steam or a mixture of these) [3]. Whey is a yellow-greenish waste liquid formed due to the clotting of milk during the cheese manufacturing process [4]. The compositional difference between whey and whey powder are listed in Table 1 [5].

Table 1. Typical composition of whey and whey powder [5]

Composition (%)	Whey	Whey Powder
Protein	0.7 – 0.8	11.0 – 14.5
Fat	0.1	1.0 – 1.5
Ash	0.5	8.2 – 8.8
Lactose	4.9	63.0 – 75.0
Water	93.7-93.8	3.5-5.0

Most of the work on hydrogen production from whey was done using biological processes such as fermentation [6-9]. Only a single report on hydrogen production through the gasification of whey was found in the literature and no reports on the gasification of whey powder were found. Muangrat et al. investigated alkaline

subcritical water gasification of whey powder solution which is 5 g of whey powder dissolved in 100 mL of deionized water. Hydrogen peroxide (1.5 wt%) was used as an oxidant. The highest hydrogen yield was obtained as 147 mg H₂ at 120 min, 390 °C and 1.67 M NaOH as a catalyst [10].

In this study, the gasification of whey and whey powders was performed to obtain hydrogen-rich gases.

2 Materials and methods

2.1 Materials

Whey and two types of whey powder were gasified in order to obtain H₂ rich gas product (Table 2).

Table 2. The content of whey and WP

Sample	Content of Whey and WP
W	Whey (5% solid material)
WP1	Whey Powder (0.05% fat)
WP2	Whey Powder (2.34% fat)

Whey was supplied from a dairy products factory in Eskisehir. The powdered samples (WP1 and WP2) were obtained by lyophilization.

2.2 Equipment

Whey (W) was gasified in a high temperature, high-pressure stainless steel, 500 mL batch reactor (PARR model 4575). Temperature and mixing speed were controlled with a PARR 4843 control unit. The maximum operating pressure and temperature of the high-pressure batch reactor was 350 bar and 500 °C, respectively. The system consists of a stirrer, gaskets, pressure gauge, and heating system. Whey powder (WP) was gasified in a 316

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stainless steel updraft tubular reactor with the dimensions of 900x10 mm. The major components of the reactor system are an insulated tubular reactor, a gas-liquid separator, and particle-moisture traps. The lyophilization process was carried out in a lyophilizer (LABCONCO) in order to obtain WP. The fat content was determined by Soxhlet extraction. 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 detector (TCD) was used to analyze the product gas.

2.3 Experimental Study

2.3.1 The lyophilization

To obtain WP, whey was lyophilized for 5 days at $-80\text{ }^{\circ}\text{C}$, under vacuum (0.180 mbar).

2.3.2 Determination of fat content

The fat content of WP was determined by Soxhlet extraction using hexane as a solvent. Extraction was carried out under reflux for 5 hours. Then the solvent was recovered by rotary evaporator under reduced pressure.

2.3.3 Gasification of whey

A high-pressure batch reactor was used for the gasification of whey with a 5.6% solid material content, using NaOH as a catalyst (0.83 M, 1.67 M, 2.51 M) at various temperatures (300, 350, 400 $^{\circ}\text{C}$) and reaction times (60, 120 min). NaOH and 1.5 wt.% H_2O_2 as an oxidant was mixed with 100 mL of whey. After the reaction, the reactor was cooled to room temperature, the product gas was collected in a gas sampling bag and analyzed by a micro-gas chromatographer. The liquid and the solid products were separated by vacuum filtration. Ethyl acetate (EA) was used as the solvent to extract the water-soluble products from the liquid sample. The solvent was removed from the EA-soluble phase using a rotary evaporator and the water content of the aqueous phase was removed through heating.

2.3.4 Gasification of whey powder

3 g of WP and 20 wt.% catalyst was dry mixed and added into the reactor. The gasification process was carried out in the presence of K_2CO_3 catalyst, at different reaction temperatures (650, 700 $^{\circ}\text{C}$) and reaction times (30, 45 min). High purity dry air was fed to the reactor as the gasification agent at 3 L/h feed rate and at 2 bar pressure. The product gas was collected in a gas sampling bag and its composition was determined using a μ -GC.

2.3.5 Gas analysis

Argon is used as the carrier gas in the MS5A column, that has an injection and column temperature of 90 $^{\circ}\text{C}$, column pressure of 35 psi, no injection delay and 180 s

analysis time. Helium is used as the carrier gas in the PPQ column, and the operating conditions of the column are 90 $^{\circ}\text{C}$ injection temperature, 70 $^{\circ}\text{C}$ column temperature, 30 psi column pressure, 50 ms injection delay and 180 s analysis time.

3 Results and discussions

3.1 Gasification of whey

3.1.1 Effect of reaction temperature

Whey was subjected to gasification at various reaction temperatures (300, 350 and 400 $^{\circ}\text{C}$) and constant reaction time (120 min) in the presence of NaOH catalyst and 1.5% wt. H_2O_2 oxidant. The change of product gas component with temperature is given in Fig. 1.

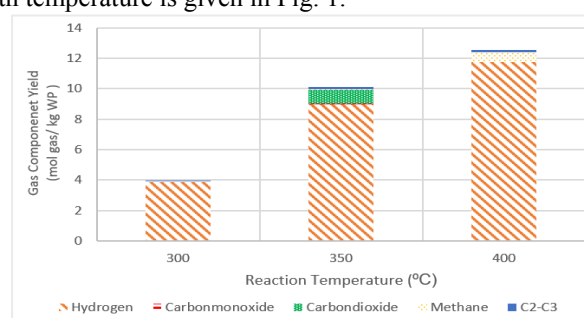


Fig. 1. Effect of reaction temperature on gaseous products (1.67 M NaOH, 120 min reaction time and 1.5 % wt. H_2O_2)

As it can be seen in Fig. 1, hydrogen yield increases from 3.85 to 11.74 mol H_2 /kg WP2 with the temperature because of the secondary cracking, water-gas, and hydrocarbon reforming reactions which are endothermic. Taba et al. have encountered similar results in their work on the effect of temperature on the gasification of various feed stock [11].

3.1.2 Effect of reaction time

The effect of reaction time on the gasification of whey was investigated at different reaction times (60, 120 min) and reaction temperature (400 $^{\circ}\text{C}$) in the presence of NaOH catalyst and 1.5% wt. H_2O_2 as an oxidant (Fig. 2).

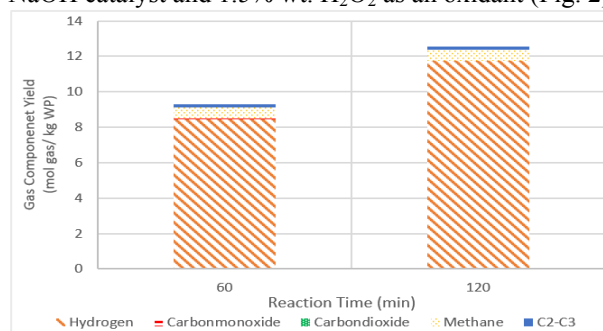


Fig. 2. Effect of reaction time on gaseous products (1.67 M NaOH, 400 $^{\circ}\text{C}$ reaction temperature and 1.5 % wt. H_2O_2)

According to Fig. 2, The hydrogen yield increased greatly from 8.44 to 11.74 mol H₂/kg WP2. Hydrogen yield increased by about 39% with the reaction time. Muangrat et al determined that an increase of hydrogen yield with increasing reaction time could be explained by the decomposition of heavier carbon-containing hydrocarbon gases taking place at longer reaction times [10].

3.1.3 Effect of catalyst concentration

Effect of NaOH catalyst concentration at constant reaction time (120 min) and reaction temperature (400 °C) and 1.5% wt. H₂O₂ oxidant was investigated. Component yields are plotted against catalyst concentration in Fig. 3.

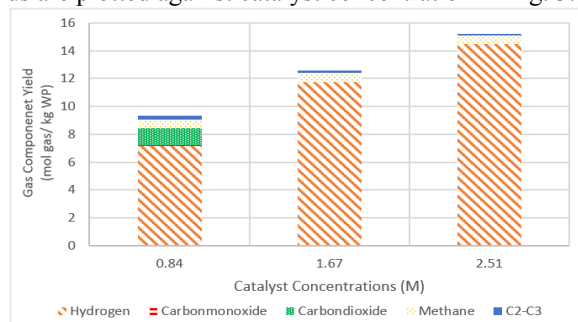


Fig. 3. Effect of catalyst concentration on gaseous products (120 min reaction time, 400 °C reaction temperature and 1.5 wt. H₂O₂)

Fig. 3 shows that the highest hydrogen yield (14.47 mol H₂/kg WP2) was obtained with 2.51 M NaOH. At these conditions, the CO₂ yield was zero. Onwudilli et al investigated the effect of NaOH on hydrothermal gasification. NaOH promotes the consumption of CO and captures CO₂. When the NaOH concentration increases, CO₂ yield decreases. The presence of NaOH shifts the water - gas reaction to the forward direction by capturing CO₂ and therefore increases the hydrogen yield [12].

3.2 Gasification of whey powder

3.2.1 Effect of WP type

Two types of WP were gasified in the presence of 20 wt.% K₂CO₃ catalyst, at 30 min. reaction time and 650 °C reaction temperature.

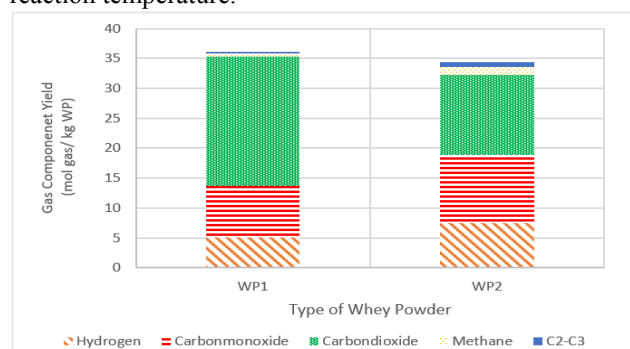


Fig. 4. Effect of WP type on gaseous products (30 min reaction time, 20 wt.% K₂CO₃ catalyst and 650 °C reaction temperature)

As shown in Fig. 4, The hydrogen yield increased from 5.12 mol H₂/kg WP1 to 7.41 mol H₂/kg WP2. Similarly, CO and CH₄ yields increased from 8.58 mol CO/kg WP1 to 11.46 mol CO/kg WP2 and 0.58 mol CH₄/kg WP1 to 1.43 mol CH₄/kg WP2, respectively. The increase of hydrogen yield can be associated with the fat content that contains high hydrogen and carbon. The fat content of WP1 and WP2 are 0.05% and 2.34%, respectively. The gasification of WP2 powder yielded more hydrogen than the gasification of WP1.

3.2.2 Effect of reaction time

The effect of different reaction times (30 min and 45 min) on the gasification of WP2 at 650 °C and in the presence of 20 wt.% K₂CO₃ was investigated. Component yields are plotted against the reaction times in Fig. 5.

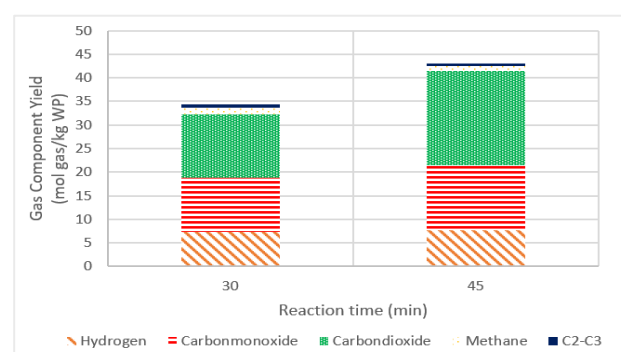


Fig. 5. Effect of reaction times on gaseous products (650 °C reaction temperature and 20 wt.% K₂CO₃ catalyst)

It can be seen in Fig. 5 that as a result of the increase in reaction time from 30 min to 45 min, H₂, CO, and CO₂ gas yields were enhanced from 7.41 to 7.71 mol H₂/kg WP2, 11.46 to 13.78 mol CO/kg WP2 and 13.36 to 19.99 mol CO₂/kg WP2, respectively. There is no significant difference between 30 min and 45 min, therefore the reaction time was chosen as 30 minutes.

3.2.3 Effect of reaction temperature

The effect of different reaction temperatures (650 °C and 700°C) on the gasification of WP at 30 min reaction time and in the presence of 20 wt.% K₂CO₃ was also investigated. Component yields are plotted against the reaction temperatures in Fig. 6.

Fig. 6. Effect of reaction temperature on gaseous products (30 min reaction time and 20 wt.% K₂CO₃)

According to Fig. 6, there is no significant difference in the hydrogen yield obtained at 650 and 700 °C. While CH₄ yield decreases with temperature, CO and CO₂ yield increases. The yield of CO increases more than CO₂ yield. It can be explained with the boudouard reaction, shifting in the forward direction with increasing temperature due to it being an endothermic reaction [13].

4 Conclusion

In this study, the gasification of whey and whey powder was investigated in order to obtain hydrogen-rich gas. The gasification of two types of WP was performed in an updraft tubular reactor. Two types of whey (5 wt.% solid content) were lyophilized to obtain the WP for gasification. The highest hydrogen yield (7.77 mol H₂/ kg WP) was obtained from WP2, which has a higher fat content than WP1, at 700 °C, with 20 wt.% K₂CO₃ and 30 min reaction time. WP2 produced the highest amount of hydrogen in the WP gasification experiments, therefore the direct gasification of whey in the high-pressure batch reactor was carried out using its whey sample. The highest hydrogen yield (14.47 mol H₂/kg WP) was obtained at 400 °C, with a reaction time of 120 min, using 2.51 M NaOH as a catalyst.

The gasification of WP solution (5 wt.% WP dissolved in deionized water) was investigated in the literature. The highest amount of hydrogen (147 mg H₂) was obtained at 120 min, 390 °C, 1.67 M NaOH as a catalyst and 1.5 wt.% H₂O₂[10]. In this study, whey with a 5.6 wt.% solid content was gasified at the same conditions and 133.4 mg H₂ was obtained. Hydrogen yield decreased by about 10.5% when whey was used directly, instead of the WP solution. Hydrogen yield was lower because whey has more impurities. It is concluded that the 10.5% decrease in hydrogen yield is preferable to the energy costs of pasteurization and spray drying processes.

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