



Co-gasification of Sorghum Hydrolysis Waste and Çan Lignite

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Abstract

In this study, it was aimed to efficiently utilize the solid waste of sorghum biomass remained after a hydrolysis process, by co-gasification with Çan lignite for high yield hydrogen production. For this purpose, steam co-gasification of the waste obtained after hydrolysis process of sorghum was with Çan lignite at a water flow rate of 0.5 mL min⁻¹ and temperature of 900 °C was performed. The gasification yields were evaluated in terms of total gas volumes and the product distributions. The results were compared with those of individual gasifications of Çan lignite and hydrolysis waste, and co-gasification was observed to have synergistic effects leading to an increase in both the produced total gas volume and the hydrogen volume.

1. Introduction

About 29% of the world's energy needs are still met by coal, and 40% of electricity is produced by coal (www.worldenergy.org). For this reason, coal is one of the main energy sources of the world. Despite the environmental problems, the amount of existing coal reserves, production costs of alternative energies, usage amounts of energy sources and extrapolations of these statistics show that, coal will maintain its place among energy resources in the future for a while (www.iea.org). Therefore, research in the coal field focuses on developing cleaner methods to reduce the negative effects, especially on environment. Gasification is an alternative technology in which coal can be processed in a cleaner way. In this method, coal is reacted with steam, air and / or oxygen, carbon dioxide or a mixture of these gases at reaction temperatures above 800 °C and converted to a mixture of synthesis gas, containing primarily hydrogen, carbon monoxide, carbon dioxide and methane (Minchener, 2005). Hydrogen production via steam gasification of coal is strong alternative for clean utilization of coal and integration of coal to the future energy technologies (Hirsch et al., 1982). Due to the low oxidation kinetics of coal char, the uncompleted transformation causes a decrease in energy efficiency in coal gasification systems. For this reason, a number of catalysts must be used to accelerate the oxidation reactions of coal (Arnolda et al., 2019). Different catalysts such as alkali and alkaline earth metal salts, transition metals and their composites are used in catalytic coal gasification processes (Lin et

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al., 2017). These minerals can be found naturally in the inorganic constituents of biomass and when coal and biomass are gasified together synergistic effects are observed due to the catalytic effects of these minerals. There are plenty of publications in the literature regarding the co-gasification of coal and biomass (Pan et al., 2000; Sjöstrom et al., 1999; Brown et al., 2000; Howaniec et al., 2011; Ren et al., 2012; Howaniec and Smolinski, 2013; Rizkiana et al., 2014; Ellis et al., 2015). As lignocellulosic biomass has complex structural and chemical mechanisms which cause resistance to deconstruction pre-treatment processes can be required before processing (Kumar et al., 2009). One of these pre-treatments is the subcritical water hydrolysis of biomass in which water is used in reaction medium so it makes the process totally environmentally friendly. The maximum solubility yields of biomass materials were found to be between 70-75% that was achieved at 250°C in subcritical water medium (Meryemoğlu et al., 2010). Co-gasification of hydrolysed biomass lead to higher gasification yields due to constructed polymer parts of the biomass to smaller oligomers and monomers so that the gasification reactions can take place easier. The inorganic salts acting like catalyst are still also in the hydrolysis solution. After hydrolysis, a solid waste remains consisting of the non-dissolved part of the biomass. The hydrolysis waste can also be co-processed by coal and if synergistic effects can be observed, the hydrolysis process is made more efficient because both the hydrolysis solution and the process waste can be utilized by gasification. Sorghum hydrolysate was co-processed with Çan lignite and synergistic effects of co-gasification were observed in our previous work (Seçer et al., 2018). In this study, we performed the co-gasification experiments of sorghum hydrolysate waste with Çan lignite at a water flow rate of 0.5 mL min⁻¹ and 900 °C, and evaluated the gasification performance in terms of total gas yield, hydrogen yield and product distribution.

2. Materials and method

2.1. Materials

In this study Çan lignite and sorghum hydrolysis waste were used as feedstock. The approximate analysis results of Çan lignite and sorghum raw biomass and sorghum hydrolysate is given in Table 1.

Table 1. Approximate analysis of sorghum biomass, sorghum hydrolysate and Çan lignite.

	Raw sorgum	Sorghum hydrolysate	Çan Lignite
C (wt %, dry)	58.6	33.8	56.3
N (wt %, dry)	4.7	4.2	1.0
H (wt %, dry)	1.4	1.2	3.8
S (wt %, dry)	-	-	5.6
O (wt %, dry) ^a	35.3	60.8	10.1
Moisture (wt %)	0.1	-	6.1
Ash (wt %, dry)	-	-	23.1
Volatile matter (wt %, dry)	nd	nd	37.6
Fixed carbon (wt %, dry)	nd	nd	39.3

*nd:not determined

2.2. Methode

2.2.1. Hydrolysis of sorghum

The hydrolysis of the biomass was carried out in sub-critical water environment under carbon dioxide pressure. 10 grams of milled sorghum was hydrolysed in a 500 mL reactor (Parr 4575 HP / TP) with 350 mL of water at 250 °C and 4060 psi. The details of the hydrolysis process were given in previous studies (Seçer et al., 2018). The hydrolysis solution was filtered and the residue (hydrolysis waste) was dried in vacuum oven and used in gasification experiments.

2.2.2. Gasification experiments

All gasification experiments were carried out in a fixed bed reactor. Coal, hydrolysis waste or coal / hydrolysis waste mixture containing 25 % waste, were prepared to be 1.0 g in total amount on dry and ash free basis (daf), and poured into a stainless steel reactor (inside diameter 0.56 " , outer diameter 1.4"). The reactor was heated to 900 °C with a heating rate of 30 °C min⁻¹ in a high temperature oven, while the water, as the gasification agent, was sent to the reactor at a flow rate of 0.5 mL min⁻¹. The gas coming out of the column was passed through condenser, and then the liquid/gas mixture was separated with a separator reservoir. The separated gas mixture was passed through a cadmium acetate solution and the H₂S was precipitated as CdS. The gas mixture were collected in a burette and then analysed quantitatively and qualitatively by Varian-450 gas chromatography instrument, with two-channel thermal electrical conductivity detector (TCD). Detailed information about gas analysis was given in previous studies (Hesenov et al., 2011).

3. Results and discussion

Co-gasification experiments of coal/hydrolysis waste mixtures were performed at 900 °C with water flow rate of 0.5 mL min⁻¹, and the results were evaluated in terms of total gas volumes and syngas product distributions in Figure 1 and Table 1. The mixtures were containing 25 % of hydrolysis waste and 75% of Çan lignite.

Figure 1. Comparison of total gas volumes obtained from different co-gasification processes (at 900 °C operation temperature and; 0.5 mL min⁻¹ water flow rate)

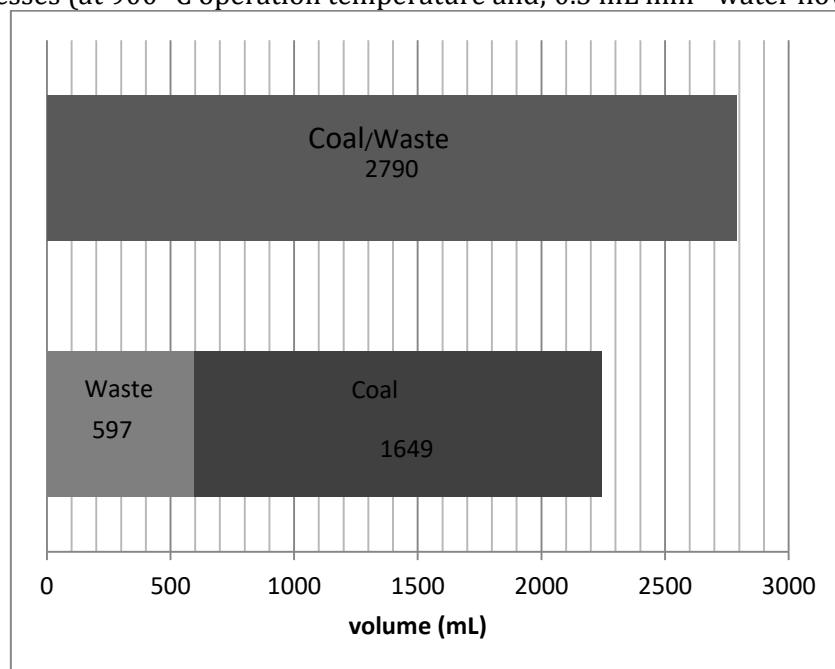
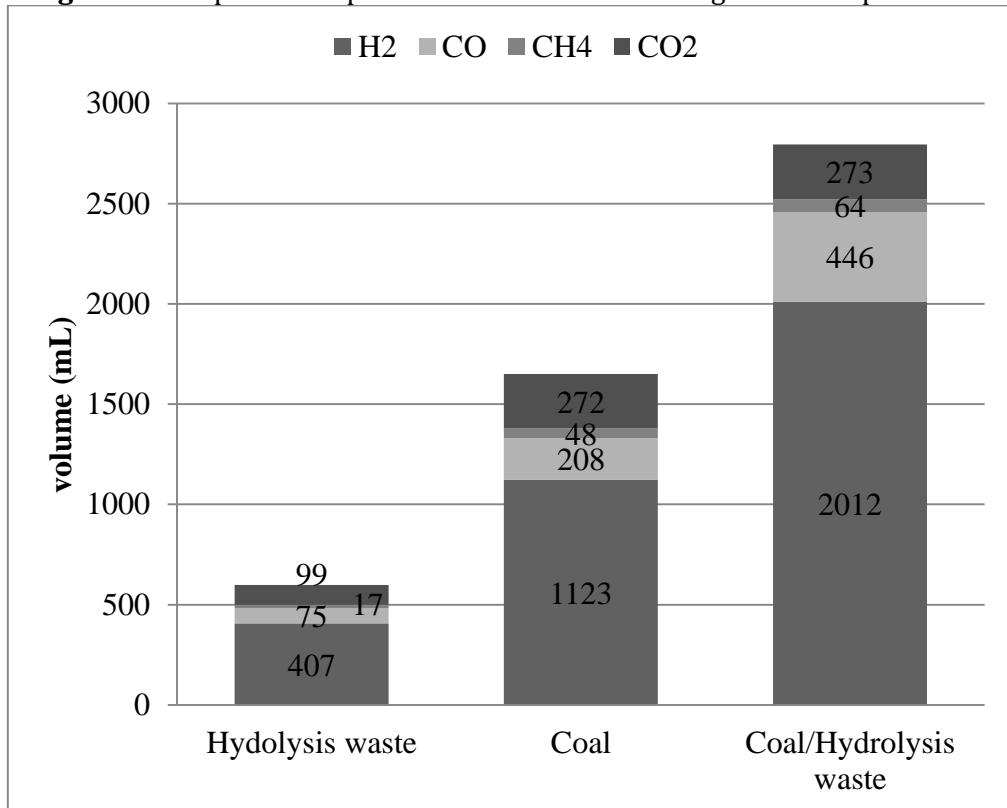


Table 1. The syngas product distributions of different co-gasification processes.

	Gas composition (%)			
	H ₂	CO	CH ₄	CO ₂
Hydolysis waste	68,3±1,1	22,0±1,0	2,5±0,3	7,2±0,8
Coal	68,1±0,8	12,6±0,6	2,9±0,3	16,5±1,2
Coal/Hydrolysis waste	72,1±0,9	16,0±0,6	2,3±0,1	9,8±0,6

Figure 2. Comparison of product volumes of different gasification processes.



The comparison of the sum of total gas volumes produced from the individual gasifications of coal and hydrolysis waste with the total gas volume produced from the co-gasification of coal/hydrolysis mixture was given in Figure 1. The results showed that the sum of total gas volumes produced from individual gasifications of the coal and hydrolysis waste (2246 mL) was less than that obtained from co-gasification of the components together (2790 mL). The percent product distributions of syngas mixtures were given in Table 1. The highest hydrogen content of syngas was obtained from co-gasification of coal and hydrolysis waste as 72.1 %. The hydrogen contents of gases of obtained from the individual gasifications of coal and hydrolysis waste were nearly same around 68%. The amounts of each component were also determined and the results were given in Figure 2. The hydrogen volume obtained from co-gasification was also higher than the sum of hydrogen volumes produced from separate gasifications of coal and hydrolysis waste. The results related with the hydrogen productions indicated the synergetic effects of co-gasification process on hydrogen production. The increasing amount of hydrogen gas is attributed to the catalytic effects of inorganic constituents of hydrolysis waste on hydrogen production reactions, primarily the water-gas shift reactions. The carbon content of hydrolysate waste is significantly higher than that of coal. Thus the carbon content of the same amounts of coal and coal/waste mixture will be different so that the carbon content of the mixture is higher. This situation leads an increase in carbon conversion reactions that result an increase in gasification yields. CO is produced by the partial oxidation reaction of carbon and the water-gas reaction of carbon with H₂O. The percent of CO in the syngas mixture, obtained from co-gasification process was 16.6 %, which is higher

than that obtained from individual gasification of coal (12.6 %). Also, the produced volume of CO was higher than sum of CO volumes obtained from individual gasifications of waste and coal. Although CO is consumed in the water-gas shift reaction for hydrogen production, the increase in carbon conversions caused the increase in the CO content of the syngas mixture as well as hydrogen. On the other hand, the CO₂ content of the gas mixture was decreased in terms of co-gasification although the amount of carbon to be gasified in was higher in the mixture. The sum of CO₂ volumes obtained from individual gasifications of coal and waste was 315 mL, while the CO₂ volume obtained from co-gasification was 273 mL. There was no significant difference in methane compositions between different gasification processes, just a little increase in methane volume was observed due to the increase in total gas formations depending on the increase carbon conversions. The co-gasification experiments of the hydrolysate solutions were also performed in previous work (Seçer et al., 2018). The gas yield of co-gasification of hydrolysate solution and coal was 3180 mL with 70.6 H₂ % which was 385 mL higher than that was obtained from coal/waste mixture.

4. Conclusion

The co-gasification experiments of coal/hydrolysate waste were performed at 900 °C with water flow rate of 0.5 mL min⁻¹. The increases in total gas volumes and hydrogen volumes obtained from co-gasification of coal and sorghum hydrolysate waste were significant indicating the synergetic effects between coal and waste during the co-gasification process. These effects were attributed to the inorganic constituents of hydrolysate waste which acted as catalysts in water-gas and water-gas shift reactions as well as the higher carbon content of the waste. Hydrolysis and low temperature gasification processes are widely used biomass processing processes. The low operation temperature of these processes is an obstacle to the complete gasification of the biomass. Therefore, it is possible that all of the biomass energy cannot be transformed since some of the biomass gasifying at low temperature is left without gasification. Utilizing of the remaining char with various methods will contribute to the total energy efficiency by ensuring that all potential energy of biomass is used. In this study, we have shown that, the waste of hydrolysis process can be utilized efficiently by co-gasification, especially for high yield hydrogen production.

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