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Feasibility and Economic Issues of Biomass Pyrolysis-Gasification: the Effect of Moisture Content of Raw Material

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The use of various wastes, such as biomass as a raw material, has significant benefits from both an emission and economic point of view. The products yield and composition, as well as the feasibility of the process, are influenced by several factors. However, the moisture content can also play an important role, because the presence of water greatly influences the chemical processes taking place and their economic characteristics.
In this work, the pyrolysis and gasification of biomass were investigated at different temperatures using different moisture content (0%, 20% and 40%) of raw material, with and without steam and catalyst. The composition of the gas products was determined by GC-FID and GC-TCD methods, and that of the solid product by CHNS analysis. In addition, using given technological layout, the process and its economic issues on the basis of feasibility were also investigated with Aspen Plus V11 software. It was found, that the moisture content of the raw material has increased the yield of hydrogen and H_2/CO ratio. Besides, with the increment of temperature the CO/CO_2 yield was increased as well. Furthermore, steam added by externally has a beneficial effect on the hydrogen and syngas yield, but it requires significant additional costs.
Keywords: biomass, pyrolysis, gasification, synthesis gas, feasibility

1. Introduction

The use of renewable energy sources has significantly increased in the past few decades owing to the caused environmental issues, the enhanced use of fossil fuels and directives (Alptekin 2022). Therefore, biomass has a key role with its carbon-neutral characteristic, renewability, wide availability and great raw material for further processes such clean hydrogen production (Safarian et al. 2019 and Aptekin 2022). The most effective way to transform biomass into valuable products is thermochemical conversion, which can be utilized with carbon-capturing technologies (Catalanotti et al. 2020). Thermochemical processes contain combustion, pyrolysis and gasification. However, the ignition produces a great amount of harmful gases aiming the heat generation, while pyrolysis is mainly utilized for liquid products. Gasification takes place at higher temperatures with or without catalysts, in the presence of oxygen/air and/or with steam implementation (Aptekin 2022). The mentioned process has five main steps which are the following drying or moisture removal, pyrolysis, combustion, cracking and reduction, where the last three take place above 650 °C. The generated products at high temperatures are mainly hydrogen, carbon monoxide, carbon dioxide and methane. However, other components and particles are involved in the gas product (Safarian et al. 2019). Regarding the gasification, there are many properties of raw material which has an effect on yield, composition and also energy requirement. Concerning the mentioned characteristics, shape, size, density, composition and moisture content are the most important ones. The latter one has a critical significance in thermochemical conversion processes. Biomass usually contains 5-35% moisture, however, having higher than 30% can cause difficulties such as problematic ignition or reducing the calorific value of the produced gas (McKendry 2002). Nevertheless, with higher moisture content remarkable heat is demanded for the gasification, water-gas shift and thermal cracking reactions (Safarian et al. 2019). Also, the temperature of reactor zones will be lower, resulting in higher water and hydrogen content, with the reduction of carbon monoxide concentration and with the enhancement of methane content (Choudhury 2015). Consequently, moisture content not only affects the composition of gas but the yield of tar.

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Raw materials with greater moisture content result in a higher amount of tar, which leads to the deposition of it in the gasifier, also tar formation can occur in the gas product (Naryanto et al. 2020).
During the gasification, the presence of catalysts can also affect the yield and the composition of gas. With a proper catalyst, the tar can be transformed into lighter products with high methane content. However, it should be mentioned, that catalysts mainly contain metals which will appear in the tar/ash causing difficulty, due to their negative effect on the environment and their expensive disposal (Papa et al. 2020).
In this study, agricultural biomass with different moisture content was investigated in thermal and thermochemical ways with steam implementation. The main aim was to investigate the effect of different moisture content on the yield, composition and required energy. Besides, a comparison was studied when the catalyst was mixed with the raw material or placed in different sections.

2. Materials & methods

In the laboratory experiments maize waste was gasificated with the investigation of the effect of moisture content, temperature, catalyst and steam. The main properties of raw material, catalyst and product analysis are summarized in the following parts.

2.1 Raw material

Based on the measurement points dried or wet, shattered (<3 mm) agricultural biomass waste (maize) was used, with the following CHNO composition 36.5 %, 5.2 %, 0.9 % and 57.4 %, respectively.

2.2 Catalyst

Throughout the measurements, Ni/ZSM-5 catalyst was used, made by wet impregnation. The method of the impregnation as well as the properties of the raw catalyst was mentioned elsewhere (Zsinka et al. 2022).

2.3 Equipment

During the measurements, one-zone tubular reactor was used at eight different temperatures (200-900 °C), with three different moisture containing raw material (0-20-40 %, 5 g), in the absence or presence of catalyst moreover steam implementation. It should be mentioned, that in dedicated measurement points the raw material and the catalyst were mixed together in case of investigating the catalytic degradability.

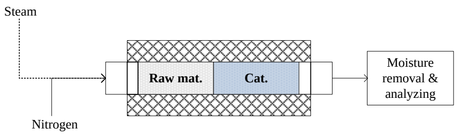


Figure 1: Schematic drawing of the equipment

2.4 Product analysis

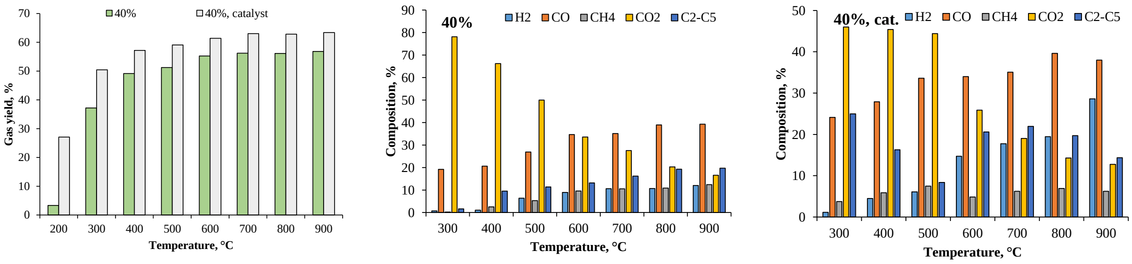
To define the composition of gas a DANI type gas chromatograph equipped with a programed injector, flame ionization and TCD detector was used. The type of the column is an Rtx-1 PONA type 100 m long column with an internal diameter of 0.25 mm and film thickness of 0.5 µm, while that of the TCD Carboxen^{TM} 1006 PLOT (30 m×0.53 mm) column was placed in the chromatograph. The analysis was performed at 35 °C isothermal condition. The detector and injector temperatures were 230 °C, while in case of TCD 120 °C with a heating rate of 15 °C/min was used. The chromatograms were evaluated using Clarity software.

3. Results & discussion

The following subsections are presenting the results in case of 0-20-40 % of moisture content, with, without catalyst and mixed with raw material. In the figures, the “0-20-40 %” means those measurement points where no catalyst and steam was implemented, while in case of “0-20-40 % cat.”, 2.5 g of catalyst and 5 g/h steam was used.

3.1 The effect of 40 % moisture content

Figure 2 (a) depicts the development of the gas yield at different temperatures. As it can be seen, with the enhancement of temperature, the yield of residue was significantly decreased while that of the gas was increased. Besides, with the presence of catalyst and steam, the residue had lower amount with 2.6-14.5 %, while the gas showed remarkable growth with values 6.6-23.8 %. However, the gas yield at 200 °C was outstandingly low, thus the composition could not be investigated. Regarding the liquid, in case of thermal degradation, the average was 32.8 %, while that of with catalyst and steam was 28.5 %. The mentioned phenomena can be explained by the water-gas shift reaction, which consumed a greater amount of moisture.



(a) (b) (c)

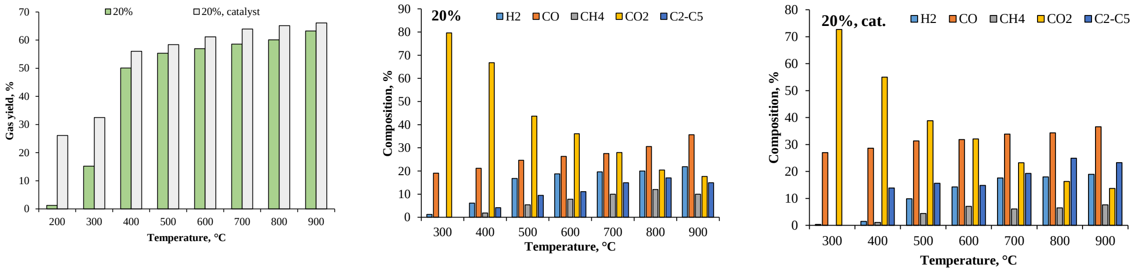
Figure 2: The change in the (a) yield of gaseous product and the composition of gas ((b)-40% moisture content, (c)-40% moisture content with catalyst and steam)

Focusing on the composition of the gas, it can be clearly observed, that during the thermal degradation, the dominating component at lower temperatures was carbon dioxide (33.6-78.2 %) and at higher carbon monoxide (34.6-39.3 %). Concerning Fig. 2 (a), the main reactions which were occurred pyrolysis, thermal cracking, Boudouard and water-gas shift reactions. At 700 °C the shifting of Boudouard reaction can clearly be seen. Regarding the hydrogen and methane yield, similarity can be observed with <12 %. Utilizing catalyst and steam (Fig. 2(b)), a similar tendency can be seen in case of carbon monoxide and carbon dioxide, however, at higher temperatures (from 600-900 °C) the hydrogen yield was notable too (14.7-28.6 %). Although the amount of lighter hydrocarbons and methane showed similar values (14.4-25.0 % and 3.7-6.2 % respectively) with the results in case of thermal degradation. Eventually, the amount of synthesis gas led to an enhancing tendency, with 88.4 mmol/g raw material at 900 °C, in the presence of steam and catalyst.
The ratio of H_2/CO is crucial for further syntheses, such as Fischer-Tropsch synthesis. This ratio has a notable effect on the overall efficiency of the process. In case of the ratios reaching value 2, the produced gas is advantageous for Fischer-Tropsch and methanol synthesis, while that of CO/CO_2 ratio, higher than 1 value is favorable for the latter one (Lee et al. 2021). Both of the H_2/CO and CO/CO_2 ratios were escalated by the increased temperature. In almost all cases, the catalytic points had higher values with 0.1-0.5 and 0.3-0.9, respectively. It should be mentioned, that the produced gas with 40 % moisture is not suitable for the Fischer-Tropsch synthesis, due to its low value, while in case of the gaseous product that arises at 600-900 °C is favorable for the methanol synthesis.
Regarding the heating value, in case of thermal measurements, an increment can be observed, due to the enhancement of carbon monoxide, methane, hydrogen and lighter hydrocarbons (with heating values 12.63, 35.95, 10.28 and 70 MJ/m^3 respectively). Focusing on the catalytic points, the heating value shows a slight decrease between 300-500 °C (up to 8.5 MJ/m^3), after taking a constant value of 22.4 MJ/m^3.

3.2 The effect of 20 % moisture content

Figure 3 (a) represents the yields obtained from raw material containing 20 % moisture. Similar observations can be made as it was in case of 40 % moisture content. The yield of residue was significantly decreased (19.7-67.1 %) with the elevated temperature, however, from 500-900 °C a slight change was noticed (up to 7 %). Regarding the gas yield, the water and catalyst implementation resulted in a greater amount (2.9-24.9 %). Besides, at higher temperatures with 20 % moisture content, a modest growth (up to 6.4 %) was obtained compared with the data in case of 40 % moisture content. Focusing on the liquid yield, the lower moisture content leads to a lower amount of liquid product (up to 18.4 %), with 21.4 and 22.2 % average value. Also, no significant difference was remarked between the thermal and thermo-catalytic points, even though water implementation and catalyst were used. This phenomenon may occur due to the high water content, which gets the catalyst wet causing a reduction in the efficiency.
Regarding the composition of gas in Fig. 3 (b), at lower temperatures, carbon dioxide is the dominant component with 79.7 and 72.7 %, respectively. In case of carbon monoxide, almost similar values were observed in the presence and the absence of catalyst (27-36.5 and 19.1-35.6%). Focusing on the yield of methane and hydrogen, their concentration was modestly higher without catalyst (with 0.8-2.4 and 1-2.9 %, respectively). Besides, the value of lighter hydrocarbons was elevated with almost 10 % in the presence of catalyst. Both phenomena can be explained by the slight decrement in the efficiency of wet catalyst. Concerning the H_2/CO and CO/CO_2 ratio, an increment was observed with the increased temperature. However, the H_2/CO was remarkably higher in the absence of catalyst and steam (with the ratio of 0.1-0.4), especially between 500-700 °C.

The opposite tendency was remarked in case of CO/CO_2 ratio, where during the thermal degradation only 0.2-2.0, while that of catalytic 0.4-2.7 was calculated. Afterward, the heating values were between 3.01-25.67 MJ/m^3, where the values obtained with catalyst and steam were higher with 0.86-6.9 MJ/m^3.

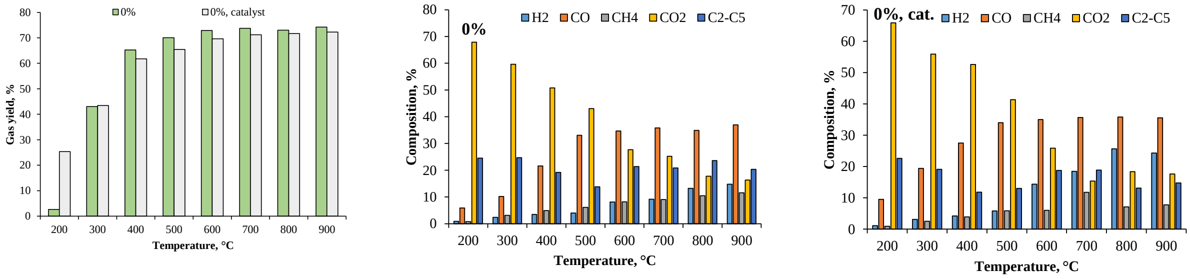


(a) (b) (c)

Figure 3: The change in the (a) yield of gaseous product and the composition of gas ((b)-20% moisture content, (c)-20% moisture content with catalyst and steam)

3.3 The effect of 0 % moisture content

Figure 4 (a) represents the yield of gaseous products with/without catalyst and steam. As it can be seen, the differences are lower than 5%, except for the yield obtained at 200 °C. However, the liquid yield was 3.8-10.06% higher with catalyst and steam, also it escalated with the increment of temperature as well as the gaseous product. Focusing on Figure (b) and (c), similarly as with 20 and 40 % of moisture, carbon dioxide was the dominant component at lower temperatures (43.0-67.9 % and 41.4-65.9 %, respectively). Besides, the amount of lighter hydrocarbons resulted in higher concentrations as it was in case of 20 and 40 % of moisture at almost all temperatures. Also, the amount of hydrogen and methane was significantly lower (Figure 4 (b) and Figure 4 (c) between 200-500 °C), which can be explained by the deficit of water content, which promotes the steam reformation and water-gas shift reactions.



(a) (b) (c)

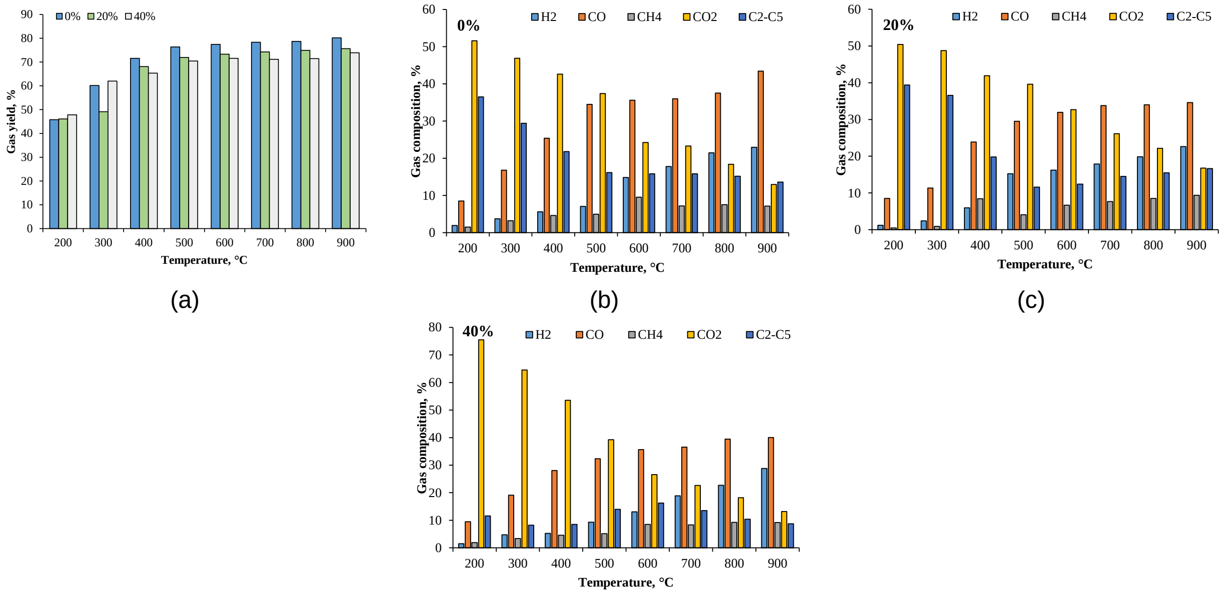
Figure 4: The change in the yield of (a) gaseous product and the composition of gas ((b)-0% moisture content, (c)-0% moisture content with catalyst and steam)

Owing to the low hydrogen yield, the H_2/CO ratio was remarkably lower than that of 20 and 40 % moisture content. At lower temperatures (between 200-500 °C), the mentioned ratio was below 0.2, while from 600-900 °C with catalyst and steam the H_2/CO ratio was increased to 0.3-0.7. Regarding the CO/CO_2 ratio, similar values were calculated (0.1-2.3) compared with the results obtained with 20 and 40 % moisture content. The heating value showed an opposite tendency, where during thermal degradation higher values (with 0.83-7.18 MJ/m^3) occurred.

Afterward, it can be noted, that the high moisture content resulted in higher amount of liquid product and residue, but had a positive effect on hydrogen yield and H_2/CO ratio, owing to the advantageous influence in water-gas shift and reformation reactions at higher temperatures.

3.4 The effect of 0-20-40 % moisture content with the mixing of raw material and catalyst

Afterwards, the effect of the catalyst was investigated with the mixing of the raw material. It is important to note, that the mixing helps in the degradation of raw material, producing more gaseous product (Fig. 5 (a)) and less liquid and residue. Regarding the yields, enhancement can be observed with the elevated temperature in case of gas and liquid yield. However, contrary to the results above, the 0 % moisture content gave the highest gas (45.9-80.15 %), residue yield 6.68-47.57 %) and the lowest liquid yield (6.63-13.17 %). This phenomenon may be occurred by the high moisture content which could prevent the efficient cracking function of catalyst.



(a) (b) (c)

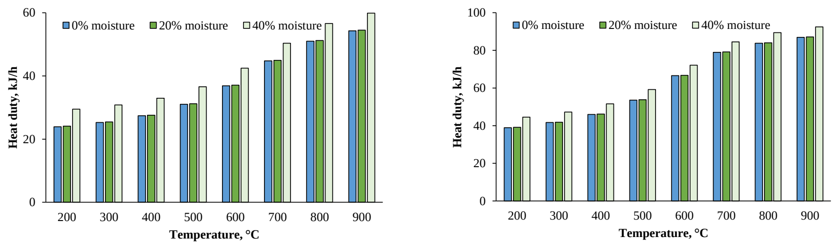
(d)

Figure 5: The change in the yield of (a) gaseous product and the composition of gas (b)-0% moisture content, (c)-20% moisture content, (d)-40% moisture content

Focusing on the composition of the gas (Fig. 5 (b)-(d)), at lower temperatures carbon dioxide and lighter hydrocarbons are the dominant components (39.6-75.5 % and 11.6-39.4 %). However, with 40 % moisture content, the value of lighter hydrocarbons is significantly lower (with 4.8-27.8 %) than that of 0 and 20 % moisture content. The mentioned phenomenon can be explained by the wet catalyst, which resulted in lower gas yield and higher amount of residue, also, it may have a slight cracking effect on raw material. At elevated temperatures (500-900 °C), the 0 % moisture content gave the highest carbon monoxide yield (34.-43.4 %) and the lowest methane yield (5.0-7.1 %). Regarding the hydrogen, raw material with 40 % moisture content resulted in the highest composition with 9.3-28.8 %, owing to the great amount of moisture content and the nickel content on the catalyst which helped in the water-gas shift reaction.
Concerning the syngas yield, the 0 % moisture content gave the highest yield with 9.5-106.4 mmol/g raw material at the mentioned temperatures, such as in case of CO/CO_2 ratio (0.2-3.4) and heating value at lower temperatures (200-600 °C, 20.66-27.66 MJ/m^3). Regarding the H_2/CO ratio the highest value was observed at 900 °C, with 40 % moisture content (0.72) but no significant difference was observed between the different moisture-containing measurement points between 200-800 °C. Despite the appropriate yields and advantageous composition of gas, the residue should be treated as harmful material, owing to the heavy metal content of catalyst.

3.5 Heat duty requirement

Besides the investigation of thermal and catalytic steam pyrolysis gasification and its comparison, the process was analyzed from an economic point of view. The net heat duty of the reactor was calculated with Aspen Plus V11, where the ultimate and proximate properties of biomass were defined. The net heat duty is the sum of the inlet heat streams minus the calculated heat duty. During the simulation, the thermal and catalytic points were simulated between 200-900 °C, with and without steam. The results can be seen in Figure 6.



(a) (b)

Figure 6: The change in the required net heat duty in the reactor (a) without steam and (b) with steam implementation

As Figure 6 depicts, the required net heat is increased by the temperature and the implemented steam, as well as with the increment of moisture content. In case of thermal degradation (Fig. 6 (a)), the net heat duties are significantly lower than that of with catalyst and steam. The greatest difference can be observed between 0 and 40 % moisture content (up to 5.6 kJ/h), while no remarkable change was noted between 0 and 20 % moisture content. In addition, the average net heat duties are 36.8, 37.1 and 42.4 kJ/h, respectively. Focusing on the measurements with steam implementation, the same tendency was observed, however the average values are notably higher (62.1, 62.3 and 67.6 kJ/h, respectively), due to the elevated amount of moisture/steam in the process.

4. Conclusions

In this work, thermal and catalytic steam pyrolysis-gasification of biomass was investigated with different moisture content between 200-900 °C. The agricultural biomass waste contained 0, 20 ad 40 % moisture. A comparison was made between the two case when the catalyst and the raw material were placed separately and mixed into the reactor. Also, the effect of steam was studied on the heating value and from an economic point of view. Regarding the yield, higher amount of gas resulted in 0 % moisture content and with the mixing of catalyst and raw material which was explained by the effectiveness of thermal and catalytic cracking reactions. However, at lower temperatures, carbon dioxide was the dominant component, while that of at higher temperatures was carbon monoxide, which can be explained by the steam gasification, thermal degradation and mainly Boudouard reactions. Nevertheless, the great amount of moisture content or water implementation helps to increase the hydrogen yield during the water-gas shift reaction. The yield of synthesis gas, H_2/CO and CO/CO_2 ratio was increased with the elevated temperature and decreased with the increment of moisture content. It should be noted, that from the mentioned characteristics, the mixing of raw material and catalyst gave the highest value. Besides, between 700-900°C the composition of gas, the H_2/CO ratio, the syngas yield and the amount of gas gave a slight difference (up to 10%), while that of CO/CO_2 ratio was more remarkable. During the economic calculations, it was stated that no significant change was observed between the values with 0-20-40% moisture content at specified temperatures. However, with the steam implementation, the required net heat value in the reactor was enhanced.

Acknowledgments

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