

Pyrolysis and Gasification of Sewage Sludge using Dolomite: the Effect of Reactor Pressure

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This paper focuses to the thermo-chemical conversion of sewage sludge into valuable products using pressure of 0.1 and 1.0 bar, and temperatures of 500 and 900°C in a tubular reactor. Both the reactor pressure and pyrolysis temperature had a significant effect on the product yields and composition. Higher gas yield was found at higher temperature and lower pressure. The lower reactor pressure resulted higher heating values of the gas fraction. Due to its significantly higher carbon monoxide content, more syngas (hydrogen and carbon monoxide) was observed using 0.1 bar pressure. Regarding the char, their composition can be also significantly affected by the reactor pressure, however their morphology differed slightly. To enhance the product yield and affect their properties natural sourced dolomite was also used. It was concluded, that the dolomite mixing into the raw material can enhanced the dry reforming reactions and increase the syngas yield.

Keywords: sewage sludge, pyrolysis, pressure, syngas, products

1. Introduction

There is not a long term sustainable way to solve the problem of increasing amount of sewage sludge; therefore their sustainable utilization is in the focus of nowadays research. However, thermal and thermo-catalytic methods seem to be a perspective direction for problem solution. By these methods, sewage sludge can be transformed into different products, such as gases, liquid fraction (bio-oil) and solid char. In general, the pyrolysis and gasification processes take place in the temperature range of 300-1000°C, usually at atmospheric pressure using an inert atmosphere (e.g. nitrogen, argon, etc.), partial oxygen or air. Depending on the reaction conditions to be used, the gas product contains hydrogen, carbon monoxide, carbon dioxide, hydrocarbons (<C₆) and other components. The liquid product of the pyrolysis is a mixture of hydrocarbons that may have a significant water content, while the solid residue is the mixtures or agglomerates of inorganic oxides, inorganic carbonates, and other carbonaceous substances [Kang et al. 2019]. It can be also said that the chemical reactions that take place during the process are significantly influenced e.g. by the temperature, the reactor configuration, the pressure, the presence of catalysts or the residence time [Soria-Verdugo 2020]. Increasing in temperature and the presence of catalysts clearly increases the amount of volatiles (e.g. gases). The main decomposition steps take place up to 500°C, while the obtained primary products can further reacted in secondary chemical reactions in the temperature range of 500-700°C. Above 750°C the amount of gases are dominant and its composition shifts toward the higher proportion of lighter hydrocarbons and hydrogen [Fonts et al. 2008]. At higher temperatures (>800°C) the ratio of CO to CO₂ as well as the amount of methane can vary significantly [Hossain et al. 2011]. For catalysts, mainly zeolites with a high specific surface area or acidic character are widely used. In addition to increasing the amount of volatile products, the catalysts can also modify their composition in a more favourable [Gao et al. 2020]. Several attempts have been made to reduce the amount of harmful components obtained in the thermal conversion of sewage sludge with catalysts [Morni et al. 2021]. The description of the effect of the pressure applied in the reactors was dealt with significantly less, than the study of the effect of the other parameters. In case where higher pressures were used, hydrogen atmosphere seems to be advantageous, because in this case, hydrogenation reactions also took place. As a result, not only the quantity of products can be modified, but also their contaminant level can be also reduced [Qui et al. 2020]. It has been observed that at higher pressures, the gas yield increased, and the CO₂ content of the products has

decreased [Yang et al. 2015]. Processes <1 bar pressure generally result in a more energy-efficient composition of the gas products [Zhang et al. 2015]. By using vacuum, the reaction time and the amount of unfavourable components caused by secondary reactions can be reduced [Zaker et al. 2021].

The goal of this work was to investigate the thermal decomposition of animal manure using different pressures in a horizontal tubular reactor. Dolomite was also used to modify the product structure and their amount.

2. Experimental

2.1 Raw materials

Animal sewage sludge (cattle manure) was used in this work. The raw material has carbon of 24.8%, hydrogen of 3.0% nitrogen of 2.9%, sulphur of 1.3%, oxygen of 45.5%, and 22.7% other elements. It has 5.9% fixed carbon, 40.6% ash content and 53.5% volatiles. To enhance the chemical reactions natural sourced dolomite was used. Based on the thermogravimetric result, the dolomite has significant weight loss from 600°C to 870°C, when the weight loss changed from 5.1% to 74.1%. At 900°C, the 25.7% of the raw material remain as char.

2.2 Pyrolysis-gasification process

Raw materials had been thermally treated in a horizontal tubular reactor at 500°C and 900°C using argon as inert atmosphere. The process layout is shown in Figure 1.

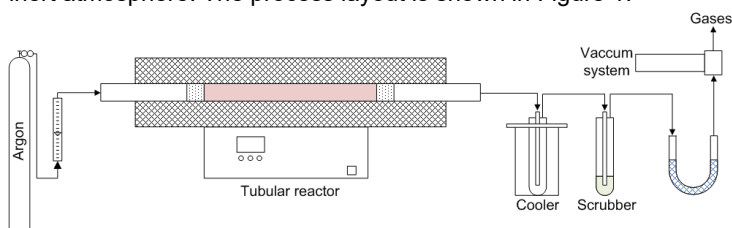


Figure 1: The process layout

Firstly, 5g of raw material was placed into the reactor, then the temperature was elevated till 500°C or 900°C with 100°C/min heating ramp. The reaction time was 30 mins after the pre-heating period. Regarding the used reactor pressure, atmospheric (1 bar) and vacuum (0.1 bar) pressure were tested. In some cases dolomite was mixed into the raw material and pyrolyzed together.

2.3 Product analysis

The composition of gases was investigated by a gas chromatography. Regarding the hydrocarbon composition DANI GC was used fitted with FID, Rtx-1 PONA type 100 m long column with an internal diameter of 0.25 mm and film thickness of 0.5 µm (the column temperature was 35°C, while the detector and injector temperatures were 230°C). The hydrogen, the carbon monoxide and carbon dioxide, and methane content of the gaseous products was investigated by DANI GC fitted with TCD detector, Carboxen™ 1006 PLOT (30m×0.53mm) column. The column space temperature was 30°C used till 18 minutes, then it was increased to 120°C (15°C/min). Finally the temperature was modified to 150°C for 2 minutes.

3. Result and discussion

3.1 Product yields

The product yield obtained at pyrolysis reactions using 0.1 and 1.0 bar pressure are summarized in Figure 1. It is important to mention, that no liquid products were found in any case, only gases and solid char remained after the thermal treatment at both temperatures. Regarding the yields of volatiles (gases), it is clear, that more gases were found at 900°C, than that of at 500°C, which was the consequence of the lower thermal stability of components at higher temperatures. The application of vacuum can enhance the gas formation, because a higher yield of gaseous products was shown under 0.1 bar pressure, than that of at 1.0 bar. Presumably, the difference in partial pressure of components at 0.1 bar and 1.0 bar could be blamed for that phenomenon. Glancing the effect of dolomite, enhancement in the formation of volatiles can be concluded, because a higher yield of gaseous products was found in the presence of dolomite, than that of in absence.

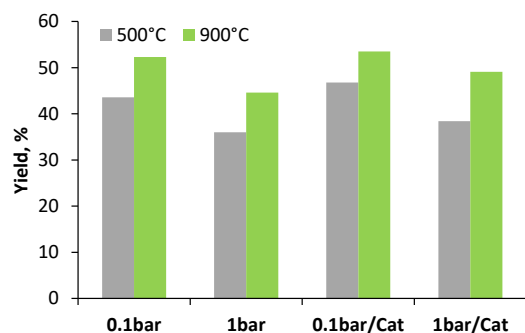


Figure 2: The yield of gases

3.2 Gases

3.2.1 Composition

The composition of gases was followed by GC-FID and GC-TCD methods (Figure 3). Based on the results, there are clear differences in the composition of the gas products obtained by the using of different operating parameters. The amount of hydrogen was significantly higher at higher temperature. At 500°C, the amount of hydrogen in the gas products was 1.7-10.4%, while at 900°C it was 14.1-25.2%. In parallel, the amounts of methane and C₂-C₆ hydrocarbons were significantly lower at 900°C, than at 500°C. The amount of carbon monoxide and carbon dioxide did not change significantly in terms of their ranges as function of temperature. The concentration range for CO was 7.9-45.0% (500°C) and 26.5-48.9% (900°C), while for CO₂ it was 1.8-5.7% (500°C) and 3.1-8.7% (900°C). Regarding the effect of pressure, it can be said that at lower pressures (0.1 bar) significantly more CO was generated in all cases, while the amount of other components was less. No clear correlations were found in the amount of C₂-C₆ components because it decreased at 500°C without catalyst, and increased in the presence of catalyst. At 900°C, both without catalyst and in its presence the amount of light hydrocarbons decreased with increasing pressure.

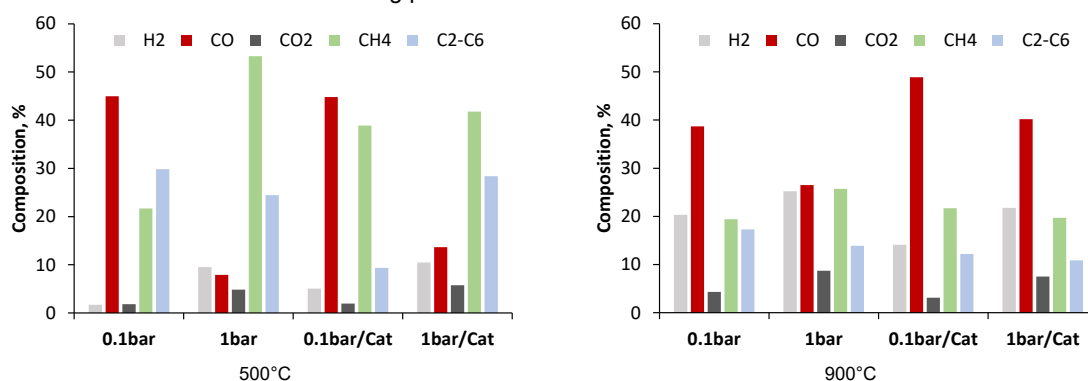


Figure 3: The composition of gases

Glancing the effect of catalyst, it can be said that at 500°C more hydrogen and CO₂ were formed in the presence of dolomite. At 900°C, opposite trend was observed, because in this case less hydrogen and CO₂ were formed in the presence of dolomite. The amount of CO was higher at both temperatures in the presence of dolomite than without it. At 500°C, using 0.1 bar in the presence of dolomite more methane and less C₂-C₆ hydrocarbons were produced, than without it. However opposite trend was observed at 1.0 bar, because in this case the amount of methane decreased, while that of C₂-C₆ hydrocarbons increased in the presence of dolomite. At 900°C, a similar trend was observed for methane as at 500°C, however, the amount of C₂-C₆ hydrocarbons was lower in the presence of dolomite than without it, regardless of the pressure. Comparing the data with Francis diagram, it is clear, that due to its higher stability the reduction in the concentration of C₂-C₆ hydrocarbons was higher than that of methane from 500°C to 900°C. Furthermore, in general methane has higher concentration than C₂-C₆ compounds.

3.2.2 Syngas yield, heating value and hydrogen/CO ratio

The syngas yield, the heating value and the hydrogen/CO ratio of gases are summarized in Figure 4. Based on the results, it is clear that the amount of synthesis gas was higher at 900°C (46.6-67.4mmol/g raw material), than at 500°C (12.5-46.6mmol/g raw material), mainly due to the formation of more hydrogen. Regarding the

effect of temperature, it can be said that the increase in the amount of synthesis gas was higher (227-268%) at a pressure of 1.0 bar than in a vacuum (45-55%). This is also due to the fact that the amount of CO at atmospheric pressure also increased significantly (275-315%) with increasing temperature. However, it is worth to mention that in the presence of dolomite, a bit more synthesis gas could be expected in the gas mixture than without it.

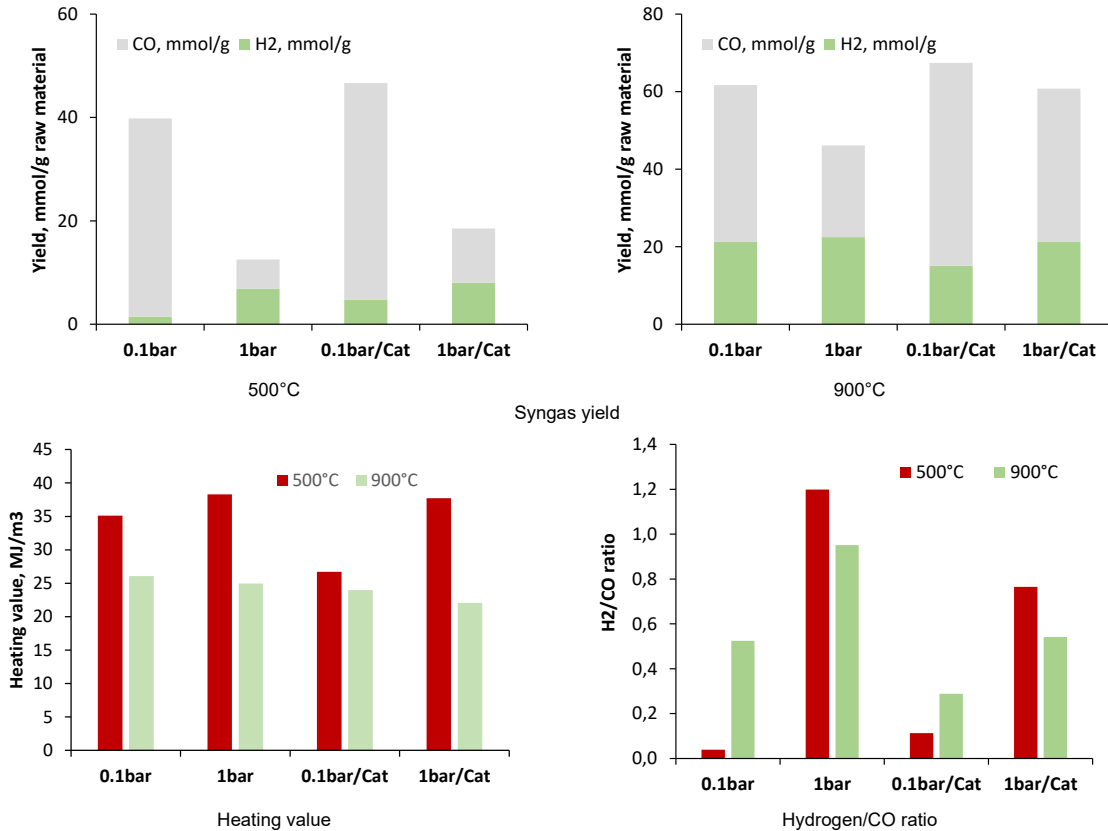


Figure 4: The syngas yield, the heating value and the hydrogen/CO ratio of gases

In terms of hydrogen/CO ratio, lower values were obtained in vacuum at both temperatures than at atmospheric pressure. The significantly more CO using vacuum was the reason for this phenomenon. To investigate the effect of temperature, it is clear that both in the absence and presence of catalyst, the hydrogen/CO ratio obtained at atmospheric pressure and at 500°C was higher, while in vacuum the hydrogen/CO ratio obtained at 900°C was higher, regardless of whether the dolomite was used or not.

Due to the higher proportion of hydrocarbons, the calculated heating values were higher in all cases for the products obtained at 500°C. However, due to the presence of more CO, lower calorific values were found at lower pressure.

3.2.3 The CO/CO₂ and hydrogen/methane ratio

Figure 5 shows the CO/CO₂ and hydrogen/methane ratios. Due to significantly more CO in gases obtained under vacuum, notably higher CO/CO₂ ratios were observed using 0.1 bar reactor pressure.

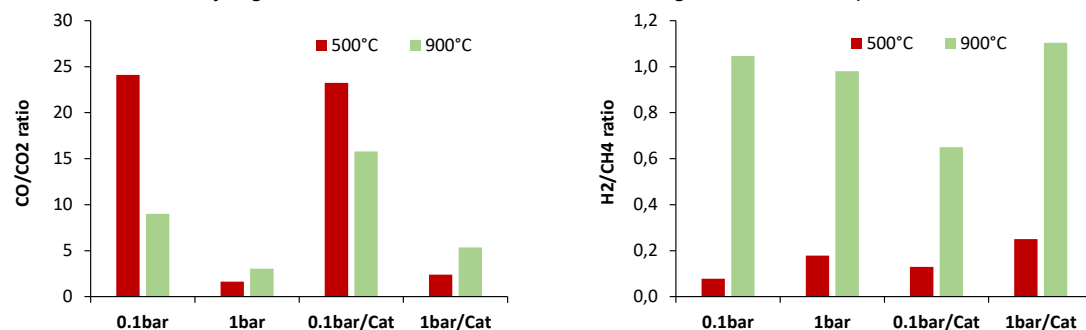


Figure 5: The CO/CO₂ and the hydrogen/methane ratio of gases

Comparing the two temperatures to be used, the CO/CO₂ ratio was significantly higher at 500°C, than at 900°C, but only when 0.1 bar vacuum was used in the reactor. At 1.0 bar reactor pressure, the CO/CO₂ ratio was higher in case of 900°C temperature. Glancing the effect of dolomite, it is also clear, that higher CO/CO₂ ratios were observed at both reactor pressures.

Regarding the hydrogen/methane ratio, due to the enhanced hydrogen formation at 900°C, significantly higher values were found independently from the reactor pressure.

3.3 Char

The elemental composition of char samples obtained at different reaction conditions are summarized in Table 1. The results well show, that the concentration of carbon increased a bit at 500°C without dolomite, while it decreased in any other cases. The hydrogen content of raw material was 3.0%, which decreased in the range of 0.32-1.72%, while the nitrogen content changed from 2.9% (cattle manure) to 0.50-3.14% (char products). When 500°C was used, the elemental composition changed only in small portion without dolomite; however the dolomite presence had a significant effect to the C, H, N and other element content. The carbon content of the chars was lower using vacuum without dolomite; however opposite trend was found in the presence of dolomite at both 500°C and 900°C. The less carbon in chars obtained at 900°C was the consequence of Boudouard reaction. Regarding the HHV, the results are correlate with the carbon content, furthermore, due to the low carbon content, it was not measureable in case of samples obtained at 900°C.

Table 1: The main properties of chars

Elements	0.1bar, 500°C	1bar, 500°C	0.1bar, 500°C dolomite	1bar, 500°C dolomite	0.1bar, 900°C	1bar, 900°C	0.1bar, 900°C dolomite	1bar, 900°C dolomite
C, %	24.5	30.4	23.1	14.6	10.5	15.9	4.6	4.1
H, %	1.7	1.4	0.8	0.5	0.3	0.4	0.9	0.8
N, %	3.1	2.4	1.8	1.0	0.7	0.9	0.5	0.9
S, %	-	-	-	-	-	-	4.4	7.7
Other, %	70.7	65.8	74.3	83.9	88.5	82.8	89.7	86.6
HHV, MJ/kg	8.06	8.17	7.77	5.87	n.a.	n.a.	n.a.	n.a.

The SEM micrographs of the chars are shown in Figure 6. As results demonstrate, the surface of the sewage sludge derived chars were amorphous containing many of particles with sharp boundary edges. There only small differences in morphology of different chars, because in some cases agglomerates with different size and shape were found. In some pictures long fibres are also visible, which was the glass wool to be used for sample placement during the pyrolysis reactions.

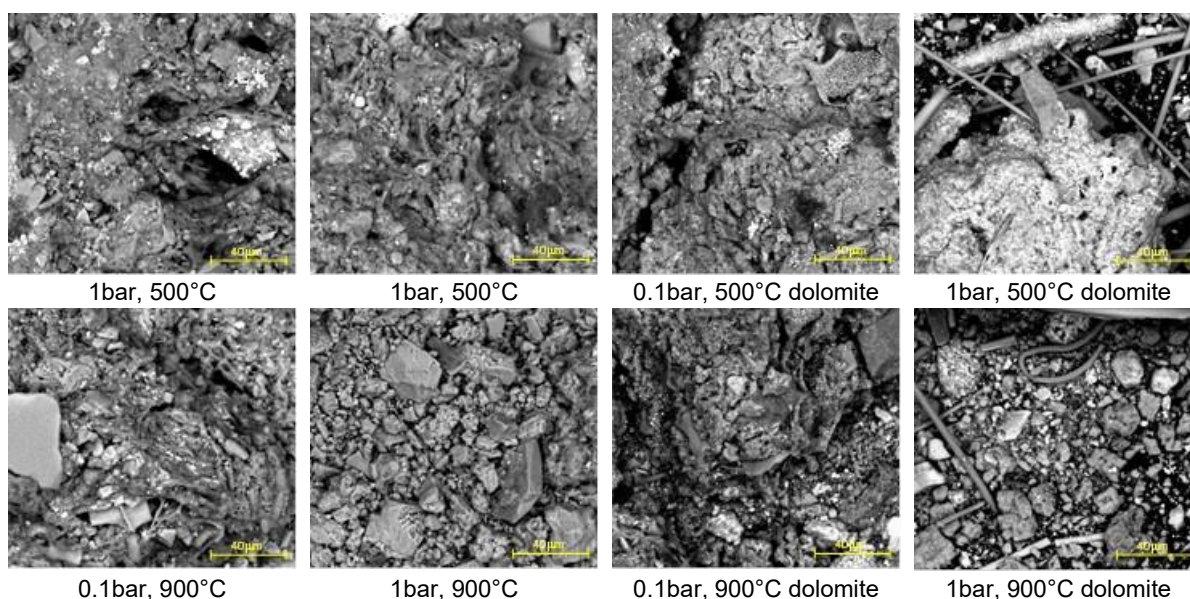


Figure 6: The SEM micrographs of sewage sludge derived char

4. Conclusions

In this work the pyrolysis of cattle manure was investigated using horizontal tubular reactor at 500 and 900°C under vacuum (0.1 bar) and atmospheric pressure (1.0 bar). In some cases, to affect the product yields and composition dolomite was used from natural source. It was concluded, that the higher temperature the presence of dolomite and the vacuum favoured to the increasing in gas yield. At 500°C, gases contained vast amount of CO using vacuum, while methane and C₂-C₆ compounds at 1.0 bar pressure. The temperature of 900°C enhanced the hydrogen production, which can be further increase by the using of dolomite. It is important to mentioned, that the lower pressure in the pyrolysis reactor decreased the concentration of hydrogen, CO and methane at both 500 and 900°C. More syngas was summarized at 900°C (46.6-67.4mmol/g raw material), furthermore, due to the more CO content, the lower pressure favored to the higher syngas yield. Regarding the hydrogen/CO ratio, lower values were found in vacuum at both temperatures than at atmospheric pressure, however, higher CO/CO₂ ratios was calculated using vacuum or lower temperature. Furthermore, the dolomite can also increase the CO/CO₂ ratio. Regarding the char, due to Boudouard reaction, significantly less carbon was measured in char obtained at 900°C, than that of at 500°C. SEM micrographs shows, that the chars looks amorphous with many of particles with sharp boundary edges.

Acknowledgments

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