

THE EFFECT OF FEEDING OF RAW MATERIAL ON GAS CHARACTERISTICS DURING THERMAL DECOMPOSITION

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Abstract: Pyrolysis and gasification are thermochemical processes that have gained significant attention in the past decades. During pyrolysis, numerous parameters can affect the final solid, liquid and gaseous products. The pyrolysis of oak wood samples at 700 °C with three different feeding times were carried out under laboratory conditions. The gas yield was the highest with the use of the lowest feeding speed (11.5 min residence time), resulting in over 20% increase in the quantity of produced gas. Faster feeding speed results in shorter residence time in the heated zone, hindering the degradation of hydrocarbon. The LHV recorded at all experiments are applicable for energy purposes. On the other hand, due to the low H₂/CO ratios (<1), none of the experiments produced syngas usable for the chemical industry.

Keywords: pyrolysis, feed rate, syngas

INTRODUCTION

The thermochemical utilisation of solid fuels dates back as far as human history. However, during the past decades, the main focus has shifted toward the use of thermochemical processes resulting in fuels with different physical states or value-added products.

Thermochemical processes include pyrolysis (thermal decomposition) and gasification. During pyrolysis, the base material is heated to 400–1000 °C temperature interval under anaerobic or anoxic conditions to carry out the thermal decomposition of the material. As a result, liquid and gaseous products are produced along with solid char, which could mainly be used for energy purposes. In case of gasification, the aim is to produce a high quantity of gaseous products from solid base materials using partial oxidation at high temperature (over 800 °C). The gas can be used as fuel of base material for the chemical industry.

The changes in the ratios and qualities of the products are regulated by numerous parameters. For both processes, temperature and residence time are significant. Higher temperature and longer residence time have a positive effect on raw material conversion: if the residence time is longer, light molecular weight hydrocarbons, non-condensable petroleum gases are produced which have considerable thermal stability [1].

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Residence time can only be regulated in continuous operation system by the changing the feeding speed of the base material, for example by increasing the rotational speed of the screw in a screw reactor the base material can be passed through the system faster. In case of batch operation, residence time refers to time interval from the beginning of heating the raw material to the time when the products are removed from the system.

Increasing the temperature can accelerate thermal decomposition, so the modification of two parameters can be used to optimise the energy consumption of the system and increase the yield of the main product.

As pyrolysis can be used independently or as a part of a gasification system, the main focus of the literature overview and the experiments was pyrolysis.

Numerous studies experimented with the effects of using different feeding systems. Singh et al. [2] examined the effect of residence time (1, 2 and 3 hours) for the pyrolysis of mustard straw at 250–500 °C in a fixed bed reactor. Based on their results, pyrolysis temperature had a more significant impact than the increased retention time for this particular raw material. Ningbo et al. [3] carried out pine sawdust pyrolysis in a screw reactor at 600 °C using 3, 4, 5, 6 and 7 minutes of retention time. It was concluded that increasing retention time reduced the quantity but increase the calorific value of the solid residue. Moreover, in case of the syngas, the longer residence time resulted in lower content of CO₂ and higher content of CO, H₂ and C₁–C₄ hydrocarbons. Ha et al. [4] carried out fast pyrolysis experiments in bubbling fluidized bed reactor at 426–528 °C temperature range using 0.8–1.8 kg/h feeding rate. The base material was wood sawdust. The increase of feeding rate from 0.8 to 1.8 kg/h during fast pyrolysis had marginal influence in the quantity of the products. Hsu et al. [5] also used fluidized bed reactor for pyrolysis of rice husk at 600 °C reactor temperature, with 10 and 20 g/min feeding rate. As a result of their experiments, it was concluded that not only the feeding speed impacted the quantity of the products, but the carrier gas flow rate, as well. With lower flow rate (30 l/min), the higher feeding rate increased the char quantity and decreased the gas yield. However, the higher flow rate (40 l/min) and increased feeding rate resulted in lower char and higher gas quantity. The reason for this was that higher carrier gas flow rate can enhance the contacts between the base material and the fluidizing glass beads. Newalkar et al. [6] pyrolyzed Loblolly pine in an entrained flow reactor at 600–1,000 °C temperature range and 5–20 bar pressure with 4 and 28 s residence time. It was concluded that longer residence time for the base material increased the residual carbon and decreases the H/C and O/C ratios of the char, especially at higher temperature (1,000 °C). The increase in temperature, pressure, and residence time decreased the concentration of C₂–C₄ hydrocarbons in the gas.

Based on the relevant literature, the effect of feeding speed can vary for each measurement. The quantity and quality of products can change because of the type and operational parameters of the equipment. Thus, the operational parameters should be modelled under laboratory conditions, first.

One of the aims of my experiments was to prepare a laboratory system applicable for pyrolysis and gasification in which batch and continuous operation. Furthermore,

experiments with different feeding speeds were carried out in the system using biomass base material, examining the possible utilisation of the produced gas.

1. MATERIALS AND METHODS

1.1. Materials and methods

Oak wood naturally dried for one year was used as a base material for the experiments, whose properties are summarized in *Table 1*.

Table 1
The properties of the base material

Average composition of the dry samples, %w/w						Original base material, %w/w
Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen	Ash	Moisture
47.79	6.19	0.11	0.01	39.98	5.92	9.26

The standard used for the elemental composition of the samples carried out with a Carlo Erba EA 1108 elemental analyser was “*EN 15104-2011: Solid Biofuels – Determination of Total Content of Carbon, Hydrogen and Nitrogen – Instrumental Methods*”. To determine the ash content, standard “*EN 14775:2010: Solid Biofuels – Determination of Ash Content*” was used, the measurement was carried out in a HK-45/12 V type heating furnace with 12 kW nominal power. The moisture content was determined using a Mettler Toledo HB43-S type moisture analyser.

Two Medingen type rotameters (3–30 and 20–260 l/h) were applied to examine the quantity of the produced gas. To be able to compare the l/h values of gas products from the different amounts of base materials, they were converted to l/1 kg base material.

The gas composition was determined with a Dani Master GC device, equipped with a TCD detector and an S/SL injector. 3 columns were connected in series for the separation of gas components: Rt-Q-bond (15 m × 0.53 mm × 20 µm), Rt-Q-bond (30 m × 0.32 mm × 10 µm) and Rt-Msieve 5A (30 m × 0.53 mm × 50 µm).

The lower heating value (LHV) of the gas mixtures was calculated using the LHVs of each component found in literature (*Table 2* [7]) using the measured concentrations.

Table 2
LHVs of gas components [7]

Components	LHV, MJ/m ³
Methane	35.949
Ethane	64.615
Ethylene	59.571
Carbon monoxide	12.680
Hydrogen	10.826

Figure 1
The experimental system for pyrolysis and gasification (a),
and the feeding process (b)

2. RESULTS

The gas production, recorded minute-by-minute, was converted to l/kg and the results are illustrated in *Figure 2*. As it can be seen in the figure, the gas production of the 700 °C pyrolysis started to decrease after 30 minutes. By the 38th minute, the gas production was below 0.5 l/h according to the rotameter, then the feeding of the base material started (with the displacement of the heated zone). In case of all three tests, the first feeding step resulted in significantly higher gas production compared to the later steps, as the time to pre-heat the base material was longer before the first displacement could start. The examination of the total feeding reveals that the increased feeding speed resulted in steadier gas production. However, this entails the decrease of the total amount of produced gas. The produced gas quantities can be seen in *Table 3*.

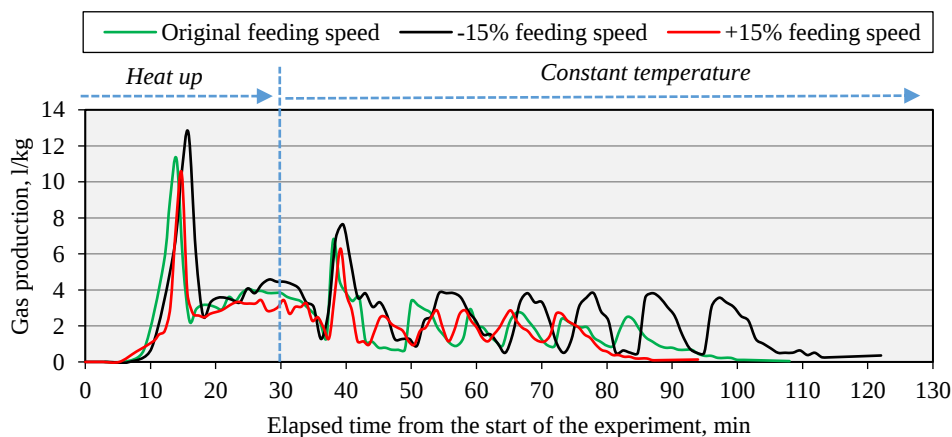


Figure 2
The effect of feeding on gas production

Table 3
The amounts of produced gas during the experiments

Experiment	-15% feeding speed	Original feeding speed	+15% feeding speed
Gas production, l/kg	253.5	207.3	200.3

The changes in the produced gas composition are illustrated in *Figure 3*. All three experimental series started with a 700 °C pyrolysis starting from room temperature, then the tests with different feeding speeds were carried out. The formation of hydrocarbons started with the temperature increase during pyrolysis. The hydrocarbons expelled the air from the reactor and CO and CO₂ was produced via combustion. With the depletion of oxygen, the amount of CO and CO₂ decreased and the release

of oxygen from the base materials led to the increase in CO content. Parallely, the amount of hydrogen increased, and the hydrocarbon content decreased until a relatively constant value was reached. During the first feeding step, there was no considerable change in the quantity of the components, as the pyrolysis of the base material could start through the prolonged holding time. However, the subsequent feeding steps had more significant effect on the gas composition. Considering the generation of the most important components for syngas utilisation (H_2 , CO and C_xH_y), the lowest feeding speed resulted in the steadiest production. Increasing the feeding speed, the hydrocarbon production remained steady, while the other components (H_2 , CO and CO_2) showed considerable fluctuation. According to the gas composition analysis, the reduced feeding speed leads to a steadier gas composition over the duration of pyrolysis.

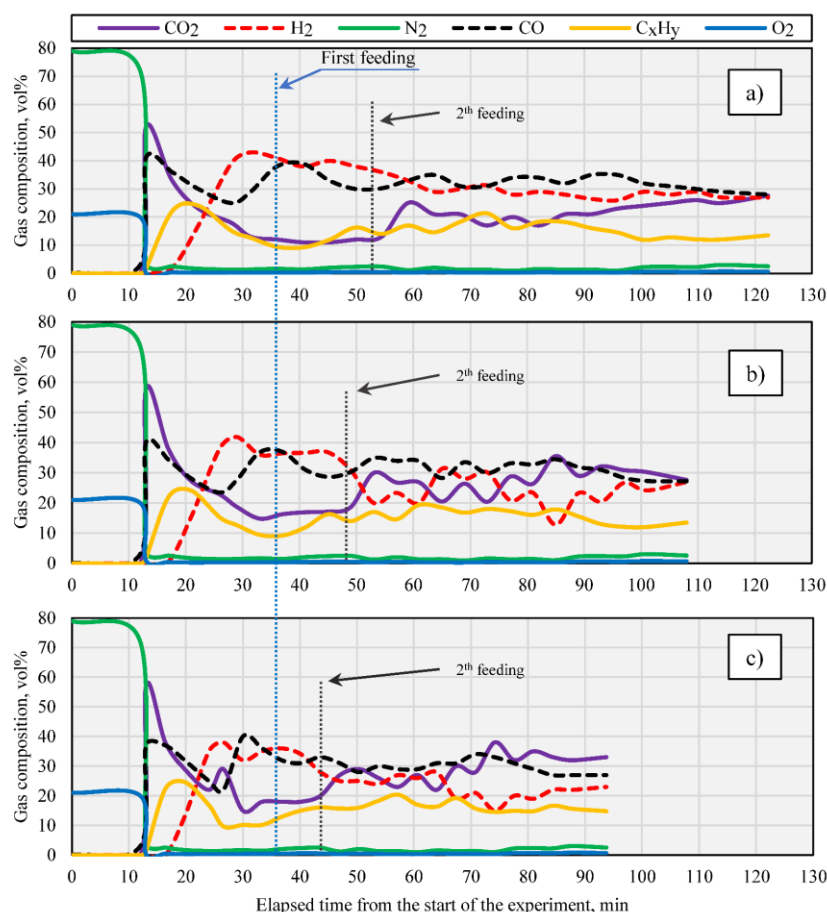


Figure 3

The changes in gas composition with -15%
(a), the original (b) and +15% (c) feeding speed

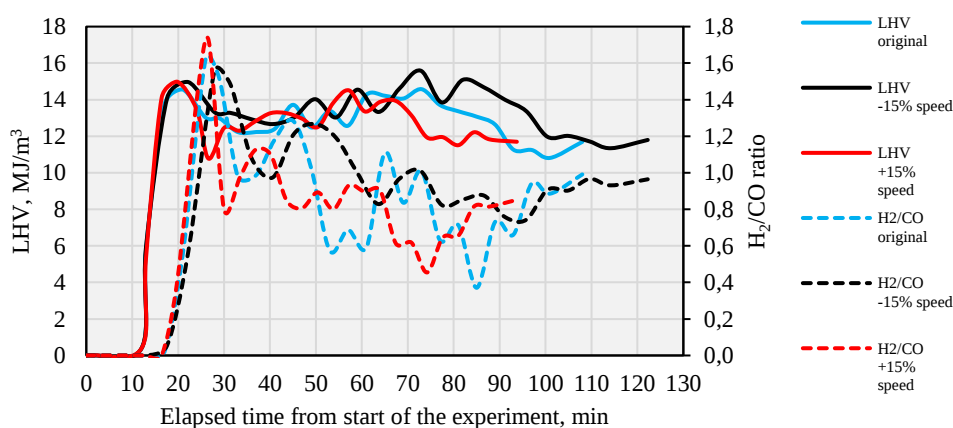
Based on the average composition of the produced gases (Table 4), increased feeding speed resulted in lower H_2 (–7%) and CO (–2%), but higher C_xH_y content (+3%). If the feeding is faster, the base material has shorter residence time in the heated zone. Thus, the rate of pyrolysis is lowered and there is no time for the further degradation of hydrocarbons.

Table 4

The average composition of the produced gases

Parameter	–15% feeding speed	Original feeding speed	+15% feeding speed
H_2	26.7	23.3	21.8
CO	30.2	29.2	28.6
C_xH_y	13.6	13.8	14.2

For energy purposes, the Lower Heating Value (LHV) of the gas is significant, while the hydrogen-to-carbon monoxide ratio can determine the possible use in the chemical industry. The changes of these values in relation to time are shown in Figure 4, and the average values during the experiments are summarised in Table 5.

**Figure 4**

The effect of feeding speed on the LHV and H_2/CO ratio of the gas

Table 5

The average LHV and H_2/CO ratios of the produced gases

Parameter	–15% feeding speed	Original feeding speed	+15% feeding speed
LHV	12.15	11.70	11.49
H_2/CO	0.84	0.76	0.73

The changes of LHV during the experiment (*Figure 4*) revealed that the LHV varied within an approximately ± 2 MJ/m³ interval during the standard feeding speed which is not a substantial deviation for using the syngas for energy purposes. On the other hand, an optimal H₂/CO ratio is necessary to produce a given chemical which would be a challenge to prepare with such a highly fluctuating ratio. Thus, the long-term gas collection and then the modification of the gas composition (H₂ addition) would be necessary for such utilisation.

Considering the total gas quantity (*Table 5*), the LHV of the gas decreased by the use of a faster feeding speed, even though the amount of hydrocarbons was higher, as stated in *Table 4*. The H₂/CO ratio also decreased with the increasing feeding speed, but the change is not significant. The lowest adequate H₂/CO ratio is 1 and can be used for acetic anhydride and acetic acid production, but all three experiments showed had syngas with lower H₂/CO ratios (0.73–0.84).

CONCLUSION

The aim of this research was to assemble a lab-scale pyrolysis system with continuous operation and study the effect of the feeding speed of raw material during pyrolysis. A laboratory system applicable for both pyrolysis and gasification, with batch and continuous operation was prepared. In the laboratory system, continuous pyrolysis tests were carried out and it was determined that the quantity and composition of the produced gas can be influenced by the feeding speed of the base material.

As the feeding speed was increased, less time was available for the pyrolysis process, decreasing the efficiency of pyrolysis. As there is no time for complete pyrolysis, gas production already starts from the fresh base material during the final phase of the gas production. This way the gas yield can be more stable. On the other hand, as increasing the feeding time results in less time for pyrolysis and lower amount of produced gas with increased amount of hydrocarbons.

Thus, decreasing the feeding speed can result in increased gas yield and a more stable gas composition over time.

Only slight changes were observed in the H₂/CO ratio of the syngas due to the change in feeding speed. However, the ratios themselves was not appropriate for chemical industrial use. The increased feeding speed resulted in slight decrease in the LHV, but based on this value, the gas could be used for energy purposes.

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