THE COMPOSITION OF GASEOUS PRODUCTS FROM CORN STALK PYROLYSIS PROCESS

by

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Original scientific paper
DOI: 10.2298/TSCI120711021D

This paper describes experimental investigation of corn stalk pyrolysis. The mass of the sample (corn stalk) inside a pyrolytic reactor was 10 g with particle diameter of 5-10 mm. The sample in the reactor was heated in the temperature range of 24-650 °C and the gas components generated during corn stalk pyrolysis were measured using gas analyzer G750 POLYTECTOR II. The sample mass before, during and after pyrolysis process was determined by using METTLER P1000 digital scale. Experimental results of the corn stalk pyrolysis indicate that as the temperature in the reactor increases from 300 °C to 650 °C, the pyrolytic gas yield increases from 60% to 72%, while the char (coke) yield decreases from 40% to 28%. In the temperature range mentioned, the CO_2 volume fraction in pyrolytic gas decreases, while the volume fraction of methane increases up to 39.5% followed with a constant decrease in the volume fraction of oxygen. The results obtained can represent starting basis for determining material and heat balance of pyrolysis process as well as corn stalk pyrolysis equipment.

Key words: *pyrolysis, corn stalk, reaction temperature, gas components*

Introduction

Biomass can be defined as biodegradable fraction of products, waste and residues from agriculture, forestry and related industries as well as the biodegradable fraction of industrial and municipal waste. Agricultural biomass consists of crops residues such as straw, corn, cob, stalks, shells, and stones. Some biomass types also carry significant proportions of inorganic species. The concentration of the ash arising from these inorganic changes from less than 1% in softwoods to 15% in herbaceous biomass and agricultural residues [1]. When we talk about biomass as a renewable fuel, we talk about plant material in the form of products, by-products, waste, and residues of the plants.

Serbia, together with all other Western Balkan countries that are interested in admittance to European Union (EU) signed Memorandum of Integration into the EU energy market. Thus, it accepted the obligation to follow EU politics and programmes. In order to achieve that, measures in stimulating electricity production by using biomass have to be adopted. In Vojvodina (region of Serbia), the most common are plant residues in agricultural production.

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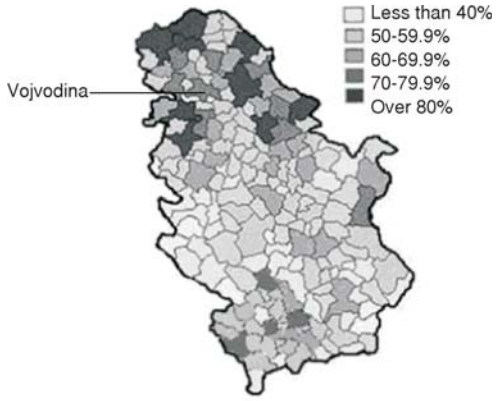

Figure 1. The geographic distribution of biomass energy potential in Serbia [3, 4]

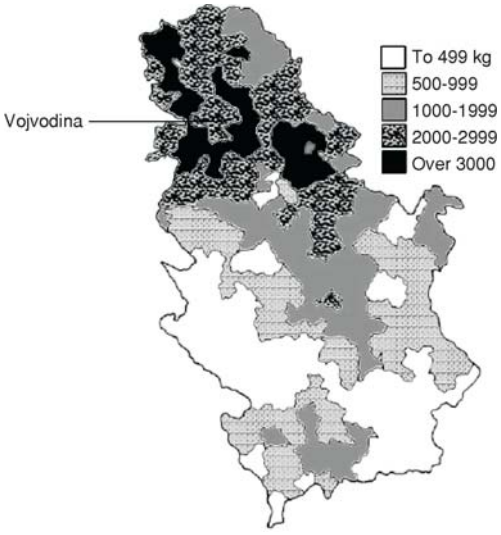

Figure 2. Map of Serbia with average corn yield per 1 ha according to the calculation for 100 ha of arable land [5]

Recently, there has been an increasing trend in oilseeds production in order to gain liquid biomass which would be used as fuel. Energy balance plan for Vojvodina predicts that the content of solid biomass, principally harvest residues, is around $35000 \cdot 10^{12}$ J of heat and 360 GWh of electrical energy per year [2].

Agricultural residues are the main biomass renewable sources in Serbia. The main area for crops production is the northern part of the country (fig. 1), with production of maize, soy, barley, rye, wheat and other (fig. 1).

Most of the arable crops are distributed all over the territory of Serbia where some crop groups have higher yields in certain areas. Corn grows in almost every part of Serbia, and especially in Vojvodina and Morava river valley (fig. 2).

There is a significant difference in the quality of agricultural biomass depending on the regions and seasons [6]. Table 1 [7] shows proximate analysis of the agricultural biomass from different regions in Serbia. The same table also shows melting temperatures of ash for the discussed biomass that are determined by using the standard SRPS CEN/TS 15370-1:2009. It can be seen that all biomass species have different mass fractions of moisture, ash and volatile matter. Judging by the value of ash melting temperature, wheat and soy straw are significantly different in the way that soy straw has high values of melting temperature, while wheat straw has lower values. This can adversely influence the combustion process of agricultural biomass and its utilization.

The main biomass thermal conversion processes are combustion, gasification, pyrolysis, and liquefaction. Pyrolysis of biomass is the heating of solid biomass in an inert atmosphere to produce gaseous products (mainly CO_2, H_2, CO, CH_4, C_2H_2, C_2H_4, C_2H_6, benzene, *etc.*), liquid products (tars, high molecular hydrocarbons, and water) and solid products (char).

Slow pyrolysis (slow heating rate) has been practiced for many years and requires relatively slow reactions at low temperatures to maximize solid char yield. A number of different approaches are being developed in order to optimize an efficient pollution-free system [8].

Liquid fuel production by fast pyrolysis is a promising technology. High yields of liquid products can be obtained under optimized conditions of pyrolysis process. Pyrolysis oil consists of water and a complex mixture of organic compounds that are condensed and collected af-

Table 1. Proximate analysis of agricultural biomass in Serbia [7]

	Soybean	Rapeseed	Wheat	Corn stalks
Moisture, W [wt.%]	8.35-39.95	8.84-18.19	8.28-9.90	7.26-9.79
Ash, A [wt.%]	3.92-15.82	3.95-5.88	5.89-12.53	2.26-5.52
Fixed carbon, C_{fix} [wt.%]	14.06-20.27	17.88-18.52	18.15-18.29	14.45-17.95
Volatiles [wt.%]	69.06-81.40	76.24-77.53	69.18-75.96	76.52-80.67
t_1 – sintering temperature [°C]	1185	1100	880	1010
t_2 – softening temperature [°C]	1310	1270	920	1040
t_3 – hemisphere temperature [°C]	1420	1400	1100	1075
t_4 – flow temperature [°C]	1450	1420	1160	1100

ter the pyrolysis step. The time and temperature profile between formation of pyrolysis vapours and their quenching influences the composition and quality of the liquid product [9].

Experimental study of biomass pyrolysis process has been carried out by many researchers. Shuangning *et al*. [10] studied the kinetics of corn stalk pyrolysis. Kinetic parameters were determined (activation energy $E = 33.74$ kJ/mol and frequency factor $k_0 = 1013$ s^{-1}) in the temperature range of 477-627 °C. Uzun and Sarioğlu [11] obtained the following values of the kinetic parameters (activation energy $E = 51.17$ kJ/mol and frequency factor $k_0 = 57.70$ s^{-1}) in the temperature range of 260-350 ºC. Besides kinetic studies, many researchers investigate pyrolysis gases yields depending on the heating rate and increase in the reaction temperature [12-16] . All the researchers show that with the increase in the reaction temperature, the yields of pyrolytic gases H_2 and CH_4 decrease. Zabaniotou and Ioannidou [14] investigate fast pyrolysis process (heating rate at 60 °C/s) of the corn stalk in the temperature range of 470-710 °C. They have shown that in the mentioned temperature range the yield of pyrolytic gases increases (30-60 wt.%), while mass fraction of solid and liquid phase decreases. The maximum value of the liquid phase is noted at 550 °C and its mass fraction value is 28 wt.%. Further increase in pyrolytic temperature leads to lower yield of the liquid phase.

The literature data on pyrolysis modeling and kinetics cannot anticipate precisely enough the yield and distribution of pyrolysis products. With the purpose of homogenizing the temperature field and heating rate of the biomass sample in the pyrolytic reactor, this paper discusses the effect of heating rate of 21 °C/min in the temperature range of 24-650 ºC on pyrolytic gas yield, which is the objective of this paper.

Experimental analysis

Raw material

Corn stalks from Vojvodina were used as the experimental sample. Technical and elemental analysis of the corn stalks was performed at the Institute of Lowland Forestry and Environment, University of Novi Sad, Novi Sad, Serbia. The results of corn stalk composition analysis are presented in tab. 2. The analysis was determined according to ASTM standards [17, 18].

Table 2. Proximate and ultimate analysis of corn stalk [19]

	Proximate analysis [wt.%]
Moisture, [W]	13.17
Ash, A*	11.52
Fixed carbon, C_{fix}	17.00
Volatiles	59.83
	Ultimate analysis [wt.%, dry basis]
Carbon, C	48.23
Hydrogen, H	8.18
Nitrogen, N	0.81
Total sulfur, S	0.18
Oxygen, O**	31.08
Lower heating value, H_d [kJkg^{-1}]	16291

* Dry basis **Oxygen content was calculated

The scheme and description of experimental facility for corn stalk (biomass) pyrolysis

The scheme of laboratory facility used for corn stalk pyrolysis and the list of measuring points (M. P.) are demonstrated in fig. 3. In fig. 4 the scheme of thermal furnace and reactor

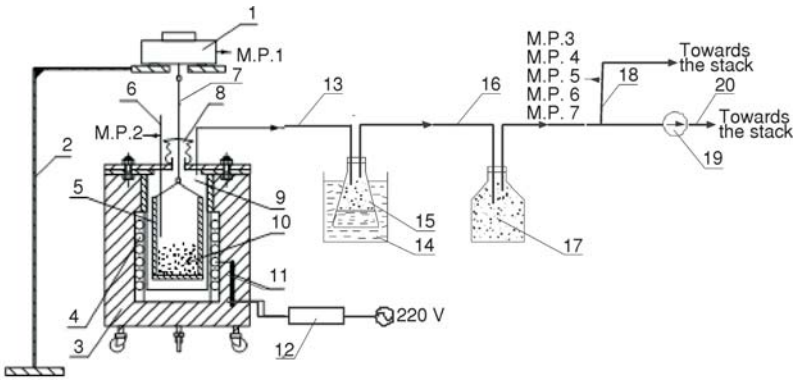

Figure 3. The scheme of experimental facility (and metering points) for corn stalk pyrolysis
1 – digital scale, 2 – scale stand , 3 – oven, 4 – electrical heaters, 5 – container for the corn stalk (biomass) sample, 6 – thermocouple (device for measuring temperature in the biomass container), 7 – flexible connection between the scale and biomass container, 8 – flexible teflon wrap, 9 – reactor vessel, 10 – corn stalk sample (biomass), 11 – temperature control sensor, 12 – temperature controller, 13 – flow of gaseous pyrolysis products, 14 – cooler, 15 – bottle for liquid phase separation, 16 – dry gaseous pyrolysis products, 17 – sampled gas (gas being analyzed), 18 – pump, 19 – gas emission into the atmosphere, 20 – towards the stack

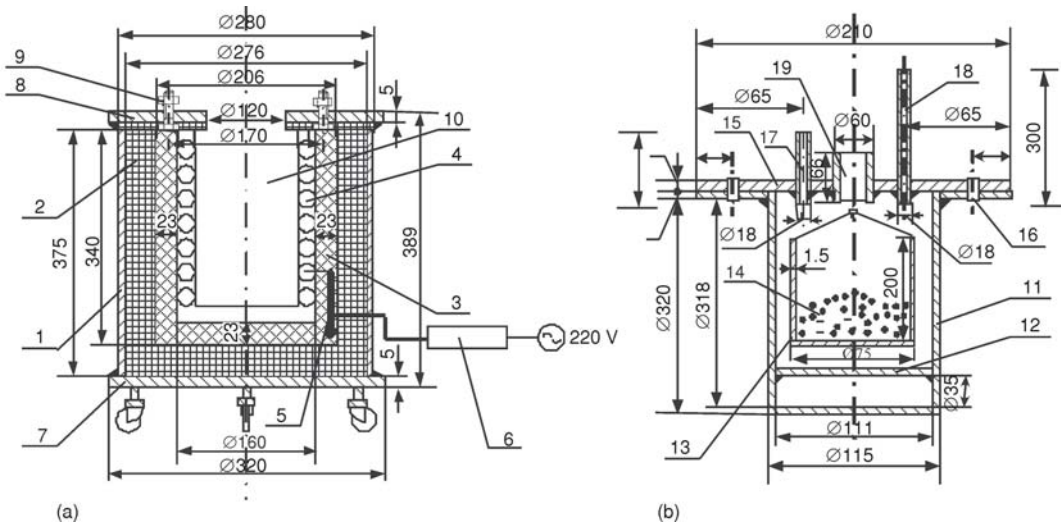

Figure 4. The scheme of thermal oven (a) and reactor vessel (b)

1 – steal cylinder, 2 – rock mineral wool (thermal insulation), 3 – chamotte, 4 – electrical heaters, 5 – temperature control sensor, 6 – temperature controller, 7 – thermal oven stand, 8 – thermal oven cover, 9 – screws for clamping the cover of the reactor vessel, 10 – reactor vessel`s position, 11 – cylindrical vessel, 12 – reactor vessel bottom, 13 – corn stalk (biomass) container, 14 – biomass sample, 15 – reactor vessel cover, 16 – screws vent, 17 – thermocouple pipe, 18 – pipe for gaseous pyrolysis products, 19 – cap with access pipe for flexible connection between the scale and biomass sample container

container for corn stalk pyrolysis is shown. The laboratory facility is designed and constructed in the Institute for Energetics, Process Technique and Protection of Environment at the Faculty of Technical Sciences in Novi Sad. During the construction of experimental facility, materials resistant to high temperatures were used as well as materials resistant to corrosion.

During the experimental investigation of corn stalk pyrolysis process, the following instruments were used:

– *Measuring the corn stalk sample mass*

Instrument: Digital scale METTLER P1000
Measurement range: 0-1000 g
Measuring error: 1000 g ± 1 g

– *Measuring the temperature of pyrolysis gas*

Instrument: Digital temperature sensor Testo 925 with type K probe (NiCr-Ni)
Measurement range: 50-1000 °C
Measuring error: ±0.2%

– *Measuring the* CO *volume share at the reactor exit*

Instrument: Gas analyzer G 750 POLYTECTOR II
Measurement range: 0-500 ppm
Measuring error: ±3 ppm

– *Measuring the H_2 volume fraction at the reactor exit*

Instrument: Gas analyzer G 750 POLYTECTOR II
Measurement range: 0-4%
Measuring error: ±0.03%

– *Measuring the CO_2 volume fraction at the reactor exit*

Instrument: Gas analyzer G 750 POLYTECTOR II
Measurement range: 0-100%
Measuring error: ±0.03%

– *Measuring the O_2 volume fraction at the reactor exit*

Instrument: Gas analyzer G 750 POLYTECTOR II
Measurement range: 0-25%
Measuring error: ±0.2%

– *Measuring the CH_4 volume fraction at the reactor exit*

Instrument: Gas analyzer G 750 POLYTECTOR II
Measurement range: 0-100%
Measuring error: ±1.0%

During the experimental investigation of corn stalk pyrolysis process, initial sample mass was 10 g with particle diameter of 5-10 mm. The aforesaid corn stalk samples were placed into the biomass sample container and then into the reactor, together with the container. The heating process was performed by using electrical heaters, and after achieving the temperature of 650 °C, that temperature was maintained within a narrow range around 650 °C for a certain period of time, until the sample mass in the reactor stabilized. The container with the corn stalk sample was attached to the scale by means of a flexible connection between the scale and the container. During the heating process, the relationship between changes in mass, temperature and time was annotated. After the experiment, char and liquid phase mass were measured.

Results and discussion of the experimental investigation

The corn stalk pyrolysis process was carried out with controlling the temperature and mass of the sample. The samples were subjected to the temperature range of 24-650 °C, and the average heating rate was 21 °C/min. Prior to pyrolysis, the biomass was shredded to fractions of 5-10 mm. In order to obtain precise results of the sample analysis, the experiment was repeated five times, and the sample had the same mass of 10 g for each experiment. The change in mass fraction m/m_0, where m stands for the sample mass that changes over time in the reactor, and m_0 stands for the initial sample mass, is demonstrated in fig. 5 as a function of reaction temperature.

As can be seen in fig. 5, there is a more significant change of mass fraction below 300 °C. That occurance is followed by the stabilization of the mass fraction m/m_0. Figure 6 shows the change in mass fraction m/m_0 as a function of reaction time.

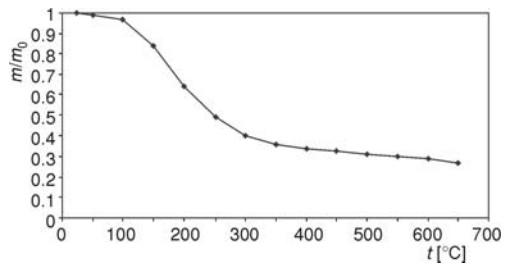

Figure 5. Mass loss curve for corn stalk sample in the temperature range of 24-650 °C (average heating rate of the sample is 21 °C/min)

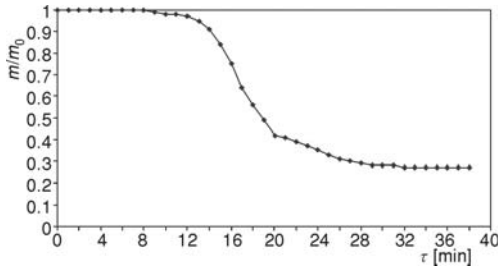

Figure 6. Mass loss curve for corn stalk sample as a function of reaction time (average heating rate of the sample is 21 °C/min)

Significant mass loss in the reactor is caused by evaporation of tar and other gaseous products. Char mass obtained by measuring after the pyrolysis process (five measurements) was in the range 2.5-2.8 g and liquid phase mass was in the range 1.9-2.4 g. The results of the corn stalk pyrolysis analysis are presented in tab. 3.

Table 3. Analysis of gas components in the pyrolysis process

Reaction temperature [°C]	CO [ppm]	H_2 [%]	CO_2 [%]	O_2 [%]	CH_4 [%]	m/m_0	Gas yield* [g]	Gas yield [wt.%]
300	>500	>4	38.0	2.1	10.5	0.40	6.00	60.0
350	>500	>4	36.5	1.9	12.5	0.36	6.40	64.0
400	>500	>4	26.0	1.6	18.5	0.34	6.60	66.0
450	>500	>4	23.4	1.4	22.5	0.33	6.70	67.00
500	>500	>4	18.6	1.0	26.0	0.31	6.90	69.00
550	>500	>4	17.2	0.9	30.5	0.30	7.00	70.0
600	>500	>4	16.4	0.7	34.5	0.29	7.10	71.00
650	>500	>4	14.6	0.6	39.5	0.28	7.20	72.00

* Gas yield was calculated by using material balance: $m_0 = m + m_{gas}$

When the reaction temperature reached 300 °C, the main gas products from the pyrolysis process were CO_2, whose volume fraction is 38% and CH_4, whose volume fraction is 10.5%. When temperature increased, the value of CH_4 volume fraction increased, whereas the value of CO_2 volume fraction decreased, along with the constant decrease of the oxygen volume fraction. When temperature increased to 650 °C, the amount of CH_4, CO_2 and oxygen accounted for 39.5, 14.6, and 0.6%, respectively (fig. 7).

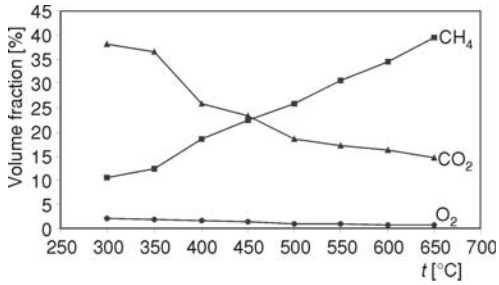

Figure 7. Variations of volume fractions of components from corn stalk pyrolysis process with reaction temperatures

Comparison between experimental and literature data

The values obtained through experimental investigation of corn stalk pyrolysis presented in this paper are tested by comparing them to the results obtained by other researchers (tab. 4). It can be observed that the values of volume fractions of pyrolysis gas components agree with the results reported in literature [12]. Small misalignment with the values obtained by experimental investigation could be explained with the fact that the literature mentioned does not contain data on the measuring error regarding the volume fraction values of the pyrolysis gas components.

Table 4. Volume fractions of the pyrolysis gas components and comparison with those reported in the literature

Reaction temperature [°C]	CO_2 [%]		O_2 [%]		CH_4 [%]	
	Experimental values	Literature data [12]	Experimental values	Literature data [12]	Experimental values	Literature data [12]
300	38.0 ± 0.03	37.2	2.1 ± 0.2	2.1	10.5 ± 1.0	11.7
350	36.5 ± 0.03	33.9	1.9 ± 0.2	1.7	12.5 ± 1.0	14.5
400	26.0 ± 0.03	26.0	1.6 ± 0.2	1.3	18.5 ± 1.0	21.0
450	23.4 ± 0.03	24.8	1.4 ± 0.2	1.4	22.5 ± 1.0	23.2
500	18.6 ± 0.03	17.6	1.0 ± 0.2	0.8	26.0 ± 1.0	27.1
550	17.2 ± 0.03	–	0.9 ± 0.2	–	30.5 ± 1.0	–
600	16.4 ± 0.03	–	0.7 ± 0.2	–	34.5 ± 1.0	–
650	14.6 ± 0.03	14.4	0.6 ± 0.2	0.8	39.5 ± 1.0	31.7

Conclusions

The experimental investigation was conducted on a corn stalk sample. The results obtained were compared to the literature data. Measured values differ only slightly from the results reported by Wang *et al*. [12] .

The analysis of pyrolysis products (tab. 3) showed that in the temperature range of 300-650 °C, the pyrolytic gas yield increases from 60% to 72%, and the char (coke) yield decreases from 40% to 28%. The volume fraction values of CO_2 decrease drastically in the temperature range of 300-500 °C and slowly at the final stage (400-650 °C). By contrast, the volume fraction values of CH_4 increase drastically in the temperature range of 300-400 °C and slowly at the final stage (400-650 °C). High yields of pyrolytic gas (60-72%) and methane up to 39.5% obtained by pyrolysis process in the envisaged temperature range (300-650 °C) and large abundance of agricultural biomass (especially corn stalk) in Vojvodina (Serbia) show promise in applying these technologies and present a possibility of substituting natural gas that Serbia is importing from abroad in large quantities.

Nomenclature

A – ash mass fraction in the corn stalk, [%]
C – carbon mass fraction in the corn stalk, [%]
C_{fix} – fixed carbon mass fraction in the corn stalk, [%]
E – activation energy, [kJmol^{-1}]
H – hydrogen mass fraction in the corn stalk, [%]
H_d – lower heating value, [kJkg^{-1}]
k_0 – frequency factor, [s^{-1}]
m – mass of the sample inside the reactor that changes over time, [g]
m_0 – initial sample mass, [g]
N – nitrogen mass fraction in the corn stalk, [%]
O – oxygen mass fraction in the corn stalk, [%]
S – sulfur mass fraction in the corn stalk, [%]
t – reaction temperature, [°C]
t_1 – sintering temperature, [°C]
t_2 – softening temperature, [°C]
t_3 – hemisphere temperature, [°C]
t_4 – flow temperature, [°C]
W – water mass fraction in the corn stalk, [%]

Greek symbols

τ – reaction time, [s]

Symbols

CH_4 – methane volume fraction in pyrolysis gas, [%]
CO – carbon monoxide volume share in pyrolysis gas, [ppm]
CO_2 – carbon dioxide volume fraction in pyrolysis gas, [%]
H_2 – hydrogen volume fraction in pyrolysis gas, [%]

Acronyms

M. P. – measuring point
SRPS CEN/TS 15370-1:2009 – Designation for standards and related documents established by the Institute for Standardization of Serbia (ISS). Solid biofuels – Method for the determination of ash melting behaviour

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Paper submitted: July 11, 2012
Paper revised: November 20, 2012
Paper accepted: January 5, 2013