

TWO-STAGE MODEL OF THE REACTOR FOR STRAW LOW TEMPERATURE PYROLYSIS

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Abstract: The scope of this paper is the definition of the most appropriate design parameters for a straw pellets torrefaction reactor of medium scale (capacity 1000 kg/h). However prior to the definition of these parameters, at subsequent level a thermodynamic tool is built and run, capable of predicting the heating value and the main characteristics (% solid residue, proximate analysis) of the torrefied straw pellets, always with parameters: the residence time and temperature.

Symbols: E – activation energy, J/(mol·K); M – mass yield, kg; K – kinetic rate, s⁻¹; t – time, s; t^* – critical time at which the second stage of torrefaction begins and dominates over the first one, s; T – temperature, K or °C; W – solid residual mass at each time step, kg.

Abbreviations: CV – calorific value; ER – energy recovery; HHV – high heating value; LHV – low heating value.

Subscripts: 0 – initial properties of biomass at $t = 0$ s; A – biomass properties during the first stage of torrefaction; B – the intermediate reaction solid product properties; C – the final torrefied biomass properties; V_1 – properties of volatiles as produced during the first phase; V_2 – properties of volatiles as produced during the second phase; raw – raw materials properties; solid – solid yield of material properties; tor – torrefaction material properties.

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Introduction

Torrefaction is a mild pyrolysis process carried out at temperatures 200...300 °C, in which biomass produces three main products: a solid product of a brown/dark color; a condensable liquid including mostly water, acetic acid, and other oxygenates, noncondensable gases-mainly CO₂, CO, and small amounts of CH₄.

The last two products are categorized as volatiles. During torrefaction the raw material loses most of its moisture and other volatiles which have a low heating value [1]. The type and amount of gas that is released during torrefaction depends on the raw material type and properties as well on torrefaction process conditions, including basically, temperature and residence time. Therefore the most important parameters, which should be taken into consideration for the design of a torrefaction unit, are: feeding material properties, temperature, residence time.

Torrefaction is used as a pretreatment step for biomass conversion into energy and heat techniques such as gasification and co-firing. The torrefaction thermal treatment not only destructs the fibrous structure and tenacity of biomass, but is also known to increase its calorific value. Also after the torrefaction, the biomass has more hydrophobic characteristics allowing the higher time storage of torrefied biomass, because of its rotting behavior. Specifically, due to the breakage of OH-groups in torrefaction process, the material loses its tendency to absorb water so it remains stable and hydrophobic. Hence, the formation of unsaturated structures is the key to preserve the torrefied biomass against the biological degradation. During the process of torrefaction the biomass partly devolatilizes, leading to a decrease of its mass, but the initial energy content of the torrefied biomass is mainly preserved in the solid product. Therefore the energy density of the torrefied biomass is higher, making it more attractive in terms of its logistic chain, i. e. transportation and management. More specifically the torrefied biomass undergoes physical changes and becomes light weighted flaky and improves grind ability.

Our goal is the definition of the most appropriate design parameters for a straw pellets torrefaction reactor of medium scale (capacity 1000 kg/h). However prior to the definition of these parameters, at subsequent level a thermodynamic tool is built and run, capable of predicting the heating value and the main characteristics (% solid residue, proximate analysis) of the torrefied straw pellets, always with parameters: the residence time and temperature.

Model

In Blasi and Lazetta study [2], the solid mass fraction $\bar{W} = W/M_0$, where W is the sample and the solid M_0 the initial mass sample is given in detail in the following Fig. 1 for wheat straw as a function of time, at several reaction temperatures. In all cases, it was observed that the heating time, the time needed to attain the reaction temperature, is always significantly shorter than the conversion time and at the time the reaction temperature's attained; only a small

fraction of the solid has undergone torrefaction. Specifically the respective ratios between the conversion and the heating time varies from a maximum of about 10...50 s (low temperatures) to a minimum of about 65 s (high temperatures).

The process become successively faster as the reaction temperature is further increased while the final solid char yield continuously decreases. Furthermore, a change in the shape of the weight loss curves appears in a limiting temperature range of 513...520 K. Indeed, for temperatures below this value, only one reaction zone is seen, whereas for larger values two different regions are observed. This can be more clearly seen in Fig. 2 where the common logarithm of the non-dimensional solid weight, defined as $P = (W - M_{C\infty})/M_0$ is reported as a function of time for wheat straw ($M_{C\infty}$ is the mass of the solid residual, left after the devolatilization (torrefaction) process is completed).

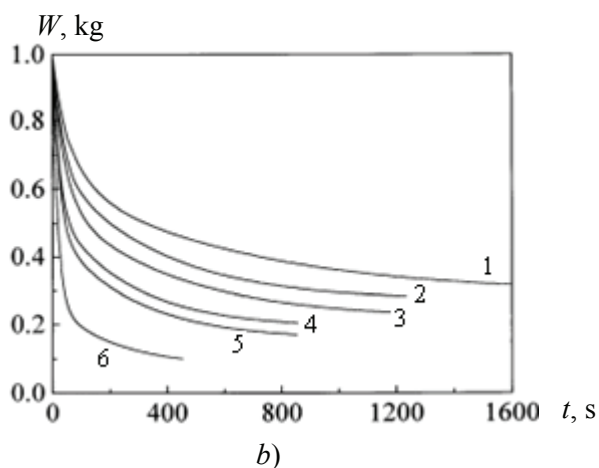
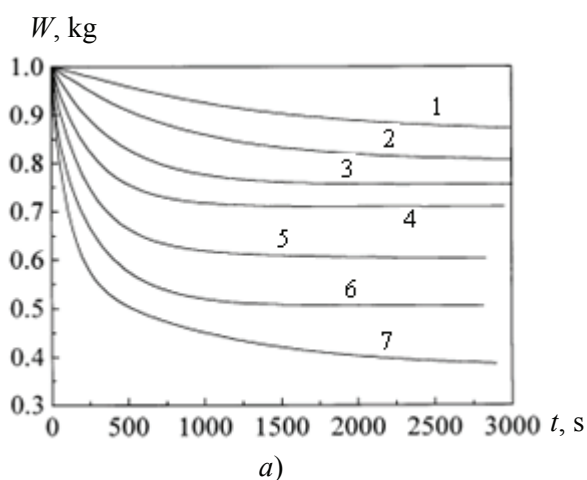


Fig. 1. Weight loss curves for wheat straw in the temperature range 400...533K (a); weight loss curves for wheat straw in the temperature range 553...648 K (b):
a: 1 – $T = 400$ K; 2 – 440; 3 – 460; 4 – 473; 5 – 493; 6 – 513; 7 – 533;
b: 1 – $T = 553$ K; 2 – 563; 3 – 573; 4 – 600; 5 – 610; 6 – 648

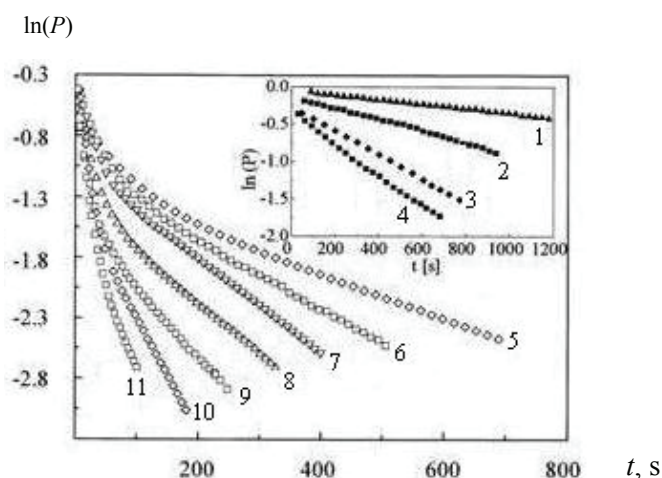


Fig. 2. Common logarithm of the nondimensional sample weight $P = (W - M_{C\infty})/M_0$:
 1 – $T = 400$ K; 2 – 460; 3 – 493; 4 – 513; 5 – 553; 6 – 573; 7 – 590;
 8 – 610; 9 – 630; 10 – 638; 11 – 648

According to it, for operation temperature above 250 °C, the torrefaction is conducted in two consecutive stages (Fig. 3):

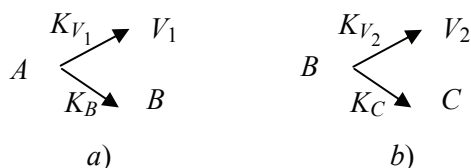


Fig. 3. Two-stage mechanism of torrefaction:
 a – stage 1; b – stage 2

where A is the initial biomass, B an intermediate reaction solid product, C the final torrefied biomass and V_1, V_2 the produced volatiles. In fact, the first stage represents the degradation of cellulose whereas the second one the degradation of semi-cellulose. The differential equations that express the mass loss or production along the time at the stage 1 are:

$$\frac{dM_A}{dt} = -K_1 M_A \Rightarrow M_A = M_0 e^{-K_1 t};$$

$$\frac{dM_{V_1}}{dt} = K_{V_1} M_A \Rightarrow M_{V_1} = \frac{K_{V_1}}{K_1} M_0 (1 - e^{-K_1 t});$$

$$\frac{dM_B^{A \rightarrow B}}{dt} = K_B M_A \Rightarrow M_B^{A \rightarrow B} = \frac{K_B}{K_1} M_0 (1 - e^{-K_1 t}),$$

where M_0 is the initial mass of biomass and $M_B^{A \rightarrow B}$ is the M_B that is generated from M_A . The corresponding kinetic rates for each stage 1 and 2 are expressed as:

$$K_1 = K_B + K_{V_1};$$

$$K_2 = K_C + K_{V_2}.$$

Table 1

Kinetic parameters

<i>i</i>	k_0, s^{-1}	$E, \text{J/mol}$
<i>B</i>	1200	53568
V_1	110000	75121
<i>C</i>	2.82	27621
V_2	1200	66541.5

An Arrhenius type temperature dependency is considered:

$$K_i = k_{0,i} e^{-\frac{E_i}{RT}}, \quad i = A, B, C, V_1, V_2.$$

The kinetic parameters according to [2] for wheat straw pyrolysis are summarized at the following Table 1.

For temperature below 250 °C only the first stage takes place. For temperature $T > 250$ °C, there is a specific time, denoted as *critical time* t^* , at which the second stage begins and dominates over the first one. At this time instant t^* , the product yield of solid *B* is denoted as M_B^* . Moreover it stands that

$$\frac{M_B^*}{M_0} = \frac{M_{V_2\infty}}{M_0} + \frac{M_{C\infty}}{M_0} = 1 - \frac{M_{V_1\infty}}{M_0},$$

where $\frac{M_{V_1\infty}}{M_0}$, $\frac{M_{V_2\infty}}{M_0}$ are the maximum amount of released volatiles at the stage 1 and 2 respectively and $M_{C\infty}$ the solid residual after the devolatilization is complete. For straw pellets, based on the literature data, both $\frac{M_{C\infty}}{M_0}$ and $\frac{M_{V_2\infty}}{M_0}$ can be calculated as a function of temperature, according to the following equations:

$$\frac{M_{C\infty}}{M_0} = 0.60 - 0.0041(T - 200) = \frac{K_C K_B}{K_1 K_2};$$

$$\frac{M_{V_2\infty}}{M_0} = 0.17 + 0.001(T - 260) = \frac{K_{V_2} K_B}{K_1 - K_2};$$

$$\frac{M_{V_1\infty}}{M_0} = \frac{K_{V_1}}{K_1}.$$

According to [1, 2] the solid residual W at the end of the process is:

$$\frac{W}{M_0} = \frac{M_A + M_B + M_C}{M_0} = \frac{M_B^*}{M_0} - \left(\frac{M_B^*}{M_0} - \frac{M_{C\infty}}{M_0} \right) \left(1 - e^{-K_2(t-t^*)} \right).$$

Mass M_A has been determined from the former stage, and M_{V_2} are calculated from the equation

$$\frac{M_{V_2}}{M_0} = \frac{M_B^* + M_A - W}{M_0} \Rightarrow \frac{M_{V_2}}{M_B^*} = 1 + \frac{M_A - W}{M_B^*}.$$

The reduction of solid M_B due to the reactions at stage 2 is:

$$\begin{aligned} \frac{dM_B^{B \rightarrow C}}{dt} &= -K_2 M_B^{B \rightarrow C} \Rightarrow M_B^{B \rightarrow C} = \\ &= M_B^* \left(1 - e^{-K_2(t-t^*)} \right) \Rightarrow \frac{M_B^{B \rightarrow C}}{M_B^*} \left(1 - e^{-K_2(t-t^*)} \right), \end{aligned}$$

where $M_B^{B \rightarrow C}$ is the residue of M_B after reaction in stage 2. Hence, the solid M_C production is easily obtained by:

$$\begin{aligned} \frac{dM_C}{dt} &= -K_C M_B^{B \rightarrow C} \Rightarrow \frac{M_C}{M_0} = K_{C\infty} \left(1 - e^{-K_2(t-t^*)} \right) \Rightarrow \\ &\Rightarrow \frac{M_C}{M_B^*} = \frac{K_C K_B}{K_2(K_1 - K_{V1})} \left(1 - e^{-K_2(t-t^*)} \right). \end{aligned}$$

The composition of torrefied biomass is determined from the corresponding correlations from literature. The torrefied biomass ultimate analysis for C, O and H is determined by the correlations from relevant studies. Similarly methodology is adopted for the proximate analysis. As far as nitrogen and sulfur prediction, it is assumed, that whole of S is remained at the torrefied solid and N goes with volatiles. Moreover, ash is totally remained at the solid part. Hence, the correlations that are applied are:

$$\frac{C_{\text{solid}}}{C_{\text{total}}} = -0.0014T - 0.010 \frac{t}{3600} + 1.22;$$

$$\frac{H_{\text{solid}}}{H_{\text{total}}} = -0.0040T - 0.020 \frac{t}{3600} + 1.87;$$

$$\frac{O_{\text{solid}}}{O_{\text{total}}} = -0.0050T - 0.015 \frac{t}{3600} + 2.02.$$

On the other hand, fixed carbon (FC) and volatiles mater (VM) are dependent on torrefaction temperature according to the following equations:

$$\frac{FC_{\text{solid}}}{FC_{\text{total}}} = -0.0003T^2 + 0.1762T - 24.149;$$

$$\frac{VM_{\text{solid}}}{VM_{\text{total}}} = -0.0122T + 3.88.$$

The vast majority of non-condensable components ‘gas’ are carbon dioxide CO_2 and carbon monoxide CO. Tito Ferro et al. [3] showed that CO_2/CO fraction is not affected from residence time but only from temperature.

The correlation that is extracted from the experimental data and incorporated to the model in terms of produced CO_2/CO fraction is:

$$\frac{\text{CO}_2}{\text{CO}} = 0.0004T^2 - 0.22T + 32.5.$$

The fraction of gas to liquid components is determined by the relevant studies [4–6]. Based on the literature data, we made the rough assumption that the gas/liquid ratio remains equal to 0.25 kg/kg.

Validation Model

This section presents the validation of the thermodynamic modeling approach, but for heating rates close to the real one in pilot and industrial scale reactors. In such units the heating rates are equal to around 10 °C/s. For the validation and the scenarios investigated in this section the experimental data presented by Prins et al. [4] are used. Unfortunately, this paper presents results for only two torrefaction temperatures, i.e. 248 and 267 °C and thus the described results are considered as validated for torrefaction temperatures greater than 248 °C (Fig. 4).

In Table 2 a fuel composition of torrefied biomass for different values of temperature is given. Since during torrefaction a devolatilization is conducted, the volatiles mass reduction is higher as the temperature increases. In addition, among the three important substances of the fuel C, H, O oxygen is released with higher rate. Finally, the increase in ash content should be also pointed out.

In a two-batch reactor, the torrefaction process is conducted in two stages with different operation parameters. The raw straw pellets enter to the first stage, are undergone to torrefaction up to a point and consecutively enter to the second batch in order the fuel pretreatment to be completed. Of course, an additional batch exists for solids cooling. A schematic view of the apparatus is depicted at the following Fig. 5.

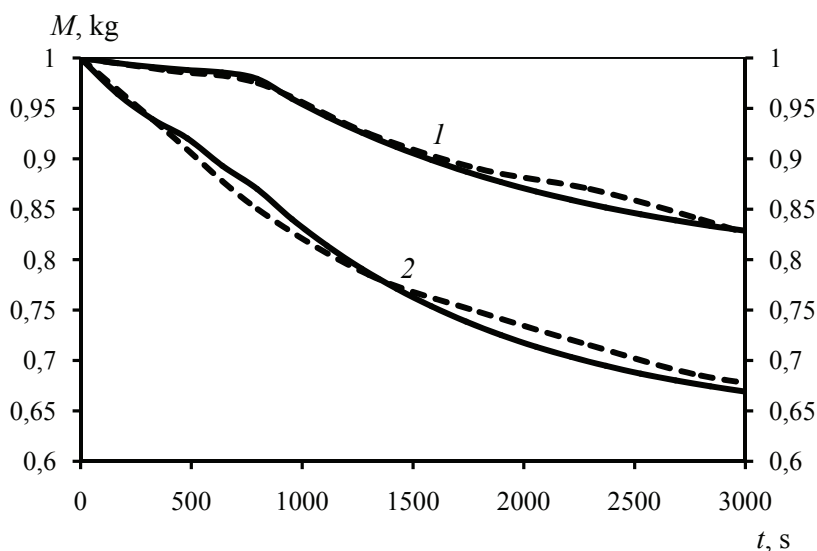


Fig. 4. Model prediction of solid mass yield in comparison with the experimental results (with dash lines), °C:
1 – 248; 2 – 267

Table 2

Fuel analysis dependence on temperature, % dry basis

$T, ^\circ\text{C}$	Proximate analysis			Ultimate analysis		
	FC	VM	ASH	C	H	O
25	19.80	71.30	11.40	43.20	5.00	39.40
240	17.66	70.50	11.84	44.95	5.32	37.88
260	30.68	56.55	12.77	46.53	5.19	35.51
280	42.59	42.69	14.71	47.85	4.98	32.46

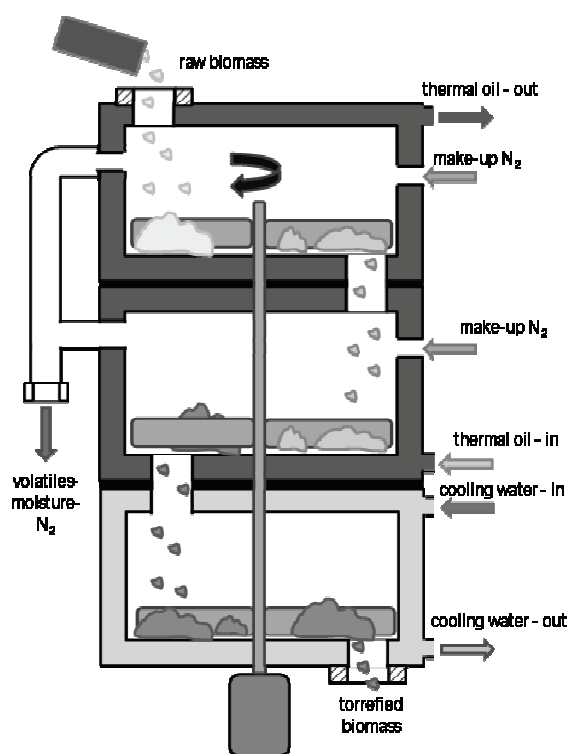


Fig. 5. Schematic representation of two-batch torrefaction reactor

In order to investigate the effectiveness of a multi-batch reactor, some case studies were ran and compared (Table 3). It is assumed the same reaction time (the residence time in each of the batch at double-batch case is the same and equal to the half of the total).

According to results of Table 3, double-batch reactor with a higher operating temperature at its first stage has a considerable advantage (higher mass yield and energy efficiency) over the single one (scenario 2). Comparing

Table 3

Comparison of single-batch and double-batch reactor effectiveness

Scenario \ Parameters	1	2	3	4
T batch 1, °C	240	260	240	260
T batch 2, °C	260	240	260	
t_1 , s	1800	1800	2000	3600
t_2 , s	1800	1800	1600	
Mass yield, %	68.11	77.62	69.15	72.09
HHV _{solid} /HHV _{raw}	1.19	1.19	1.19	1.13
Efficiency, %	81.20	92.53	82.43	81.62

the one-batch scenario 4 with scenarios 2 and 3 similar final results are observed. It makes clear that the division of the process in two steps has beneficial effect only if the second batch is operating at a smaller temperature than the first one.

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**Двухстадийная модель реактора
для низкотемпературного пиролиза соломы**

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Ключевые слова и фразы: биомасса; модель; отжиг; реактор; солома.

Аннотация: Целью данной работы является определение наиболее оптимальных параметров конструкции реактора средней мощности (производительность 1000 кг/ч) для отжига соломенных гранул. Для определения этих параметров построена термодинамическая модель процесса, способная описать основные характеристики (содержание фиксированного углерода, химический состав) термически обработанных гранул соломы в зависимости от продолжительности обработки и температуры процесса.

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