Article

Carbon Dioxide Gasification Kinetics of Char from Rapeseed Oil Press Cake

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Abstract: Rapeseed oil press cake (RPC) is an abundantly available and renewable agricultural waste material for the production of fuels or chemicals. In this study, the rates of carbon dioxide gasification of rapeseed oil press cake char were measured by thermogravimetric analysis measurements performed at various temperatures (800–900 °C) and CO2 mole fractions (0.10–1.00). The char was obtained by slow pyrolysis, where the dried RPC was decomposed at a temperature range of 1000 °C to obtain char free of impurities that can affect the measurements. The random pore model appeared to be suitable for describing the effect of conversion on the reaction rate. The temperature, CO2, and concentration dependence of the reaction rate were given by the Arrhenius equation and a power law (nth order) correlation. The kinetic parameters based on the experimental data were determined by a two-step estimation procedure. For the experimental conditions employed in this study, the parameters E and n were 222.1 kJ/mol and 0.57, respectively.

Keywords: CO2 gasification; kinetics; rapeseed oil press cake; TGA

1. Introduction

Rapeseed oil press cake (RPC) is a byproduct of rapeseed oil production that is abundant in proteins and fiber; therefore, RPC is commonly used as an animal feed. However, the high demand for rapeseed oil in Europe, particularly in Poland, leads to production of large amounts of RPC and creates opportunities for other uses. RPC is a carbon- and oxygen-rich material that can be utilized as an energy or chemical source. Among the available technologies used to transform RPC into useful products, thermochemical methods, such as pyrolysis, gasification and direct combustion, are the most popular and convenient [1,2]. In pyrolysis, a thermal decomposition of carbonaceous material at elevated temperatures in the absence of oxygen leads to the production of three fractions of products: non-condensable flammable gases, a liquid fraction that contains aqueous and organic (bio-oil) phases, and a carbon-rich solid residue—char. The product distribution in pyrolysis is strongly affected by the final temperature, the vapor residence time in the reactor (reactor type), and the heating rate. There are two primary types of pyrolysis processes, slow and fast, that have been developed for maximizing the yield of the bio-oil fraction of the products [1,3].

The pyrolysis of RPC has been examined by many investigators [1,4–11], and results concerning the effects of final pyrolysis temperatures [5,8], heating rate [4,7,12], raw material particle size [8], carrier gas flow rate in fixed bed reactors [4,6], and catalytic vapor upgrading [6] on the product distribution and its chemical composition have been reported. At the optimal bio-oil production slow pyrolysis temperature of 500 °C performed in fixed bed reactors, the yields of non-condensable gases and solid residue were 33–39 and 8–12 wt.% of the initial mass converted, respectively [1,5,8]. The remaining mass was converted into liquid product containing water and bio-oil (35–38 wt.% of the
sample mass). It was also found that the mass yield of the gas product increased at the expense of decreasing amounts of liquid and char with increasing pyrolysis temperature.

The conversion of RPC into a liquid form by a fast pyrolysis process in a lab-scale reactor was investigated by Smetsa et al. [7]. These researchers found that, at 550 °C, the oil fraction reached a maximum yield of 42.1 wt.% of the initial sample mass, approximately 17 wt.% remained as a char, and the yield of the gas fraction was 24.1 wt.%. Thus, regardless of pyrolysis conditions, a certain amount of char is produced. This material is highly reactive and can be used as a fuel or gasified with steam or carbon dioxide or their mixtures to produce clean synthesis gas suitable as feedstock for methanol, synthetic natural gas or Fischer–Tropsch synthesis [13–15].

Raw biomass can also be gasified in a one-stage process to produce fuels or syngas in the presence of a gasifying agent (usually oxygen below the oxidation stoichiometric ratio, steam, or CO₂) [16]. The process of char gasification using CO₂ promotes the production of CO, while steam gasification promotes the evolution of CO and H₂. The use of CO₂ as a gasifying agent has several advantages, as there is no requirement of energy for vaporization, the H₂/CO ratio in syngas can be readily adjusted, and the recycling and recovery of carbon dioxide is possible for realizing carbon capture and storage [17]. However, a disadvantage of gasification plants is the high operation cost due to high energy consumption.

In the one-stage gasification process, both biomass pyrolysis and char gasification take place in the same reactor. Of those two steps, char gasification is the rate-limiting step that determines the residence time required to complete the process [18]. Thus, the modeling and design of a gasifier for thermochemical processing of biomass or a reactor for char gasification requires knowledge of reliable reaction rate equations.

This paper provides information about the thermochemical conversion of rapeseed residues by means of high-temperature treatment, slow pyrolysis, and CO₂ gasification of produced char. Thermogravimetric analysis of the CO₂ gasification of RPC char was carried out for kinetic purposes. To date, there are no experimental data or rate equations on the gasification of RPC-derived char available in the published literature.

2. Kinetics of Gasification Reactions of Char

Assuming that the gasification of solids is a one-step reaction in the kinetic control regime, the fractional conversion of a solid material, X, is given by Equation (1) [19]

\[
\frac{dX}{dt} = r_s(y_g, T)F(X)
\]  

(1)

where \( r_s \) is the intrinsic reaction rate, including the effect of the gaseous reagent concentration in the gas phase, \( y_g \), and the effect of temperature, \( T \), whereas \( F(X) \) is a structural term describing the changes in the available internal surface and structural properties of the solid as the reaction proceeds. The gasification of the solid particles can be represented through different \( F(X) \) terms. The models most commonly applied to study the gasification of coal and biomass chars are the pseudo-homogeneous volumetric model (VM), the shrinking core model (SCM), also known as the grain model, and the random pore model (RPM). The specific equations arising from the use of these models for a spherical solid particle with an initial surface area \( S_0 \) are presented in Table 1.

The VM describes a process in which a chemical reaction occurs in the entire particle volume, and in the case of the first-order kinetics, the reaction rate decreases linearly with conversion (see Table 1).

If the porosity of the solid that has not reacted is very small and the solid is not permeable to gas, the reaction only takes place on the surface of the solid. As the process progresses, the unreacted core of the particle is constantly reduced, and the reaction surface and its rate decrease. The formulas given in Table 1 for the SCM are valid when the gas reagent diffusion rate through the ash layer is high compared to the reaction rate.
Table 1. Equations of the reaction rate models for gas–solid reactions [20].

| Model   | VM               | SCM               | RPM               |
|---------|------------------|-------------------|-------------------|
| $F(X)$  | $1 - X$          | $S_0 (1 - X)^{2/3}$ | $S_0 (1 - X)^{2/3} \sqrt{1 - \psi \ln(1 - X)}$ |

Integral form of rate equation, $T, y_g = \text{const}$

| $\Phi$  | $- \ln(1 - X)$  | $1 - (1 - X)^{1/3} = k_t t$ |
|---------|-----------------|-----------------------------|

Rate constant, $s^{-1}$

| $k_i = r_s = k(T)y_g^{	ext{p}}$ | $k_s = r_s S_0 = k(T)y_g^{	ext{p}}$ | $k_i = r_s \frac{S_0}{1 - \epsilon_0} = k(T)y_g^{	ext{p}}$ |

Effect of temperature

$$k(T) = A \exp \left( - \frac{E}{RT} \right)$$

The random pore model was proposed for porous solid materials, which allows intraparticle gas penetration and subsequent particle structural changes. To describe the structural changes, the model has an additional parameter, $\psi$, that characterizes the initial char structure and is defined as:

$$\psi = \frac{4\pi L_0 (1 - \epsilon_0)}{S_0^2}$$

A characteristic feature of the RPM which is not found in the other two models is that it predicts a maximum reaction rate as the reaction proceeds due to the competing effects of the growing porosity and the shrinking surface area available for the reaction. In the cases of the VM and the SCM, the reactivity of char decreases monotonically with the reaction progress [21].

As shown in Table 1, the temperature and carbon dioxide concentration dependence of the intrinsic rate constant $k$ is given by the Arrhenius equation and a power law ($n$th order) correlation, which is a simplification of the Langmuir–Hinshelwood kinetic equation normally applied for low concentrations of CO [22].

3. Materials and Methods

The rapeseed press cake after pressing sample was taken from a Polish biotech plant and was employed for pyrolysis experiments and char preparation. The RPC was previously dried in an oven at 105 °C for 24 h and ground into powder in a Pulverisette 15 mill Fritzsch. An elemental analyzer (CE Instruments NA 2500) was used to determine the carbon, hydrogen, sulfur, and nitrogen contents, and a TGA/SDTA851 LF (Mettler Toledo, Greifensee, Switzerland) apparatus was used for thermogravimetric analysis. The results of proximate and ultimate analyses of the RPC are shown in Table 2. As seen from the data, the investigated RPC contained 6.9 wt.% moisture and approximately 8.0 wt.% ash after drying. The higher heating value (HHV) and the lower heating value (LHV) of the RPC were 19.1 MJ/kg and 18.4 MJ/kg, respectively. These results do not differ significantly from those found in the literature for similar materials from different sources [6–10]. The presence of ash in the biomass (up to 8 wt.%) would be responsible for heating value reduction, in spite of the possible residual presence of rapeseed oil.

Char for the gasification experiments was prepared by devolatilization of the RPC in a horizontal fixed-bed reactor heated by an electric furnace. The samples of dried and ground cake were heated from ambient temperature to 1000 °C at a constant rate of 20 °C/min, maintained at the final temperature for 60 min, and then cooled to room temperature. Samples were heated and cooled under flowing argon at a rate of 100 cm³/min. The produced char was sieved, and the fraction of the char particles with a diameter of 70–125 µm was used for gasification experiments. The size of the char grains and the temperature range for kinetic measurements were determined on the basis of preliminary tests performed in the thermobalance, where samples of different granulation were heated in an equimolar mixture of CO₂/Ar (see Figure 1). The graph shows that the size of the char particles affects the reaction rate because higher temperatures are required to obtain similar gasification rates for larger particle.
size fractions. It should also be noted that the weight loss visible on the TGA curve below 200 °C was probably caused by the evaporation of moisture, which had already been adsorbed in the char after its preparation.

Table 2. Physical and chemical composition of rapeseed oil press cake (RPC) and RPC char (in wt.%).

| Physical Composition (wt.%) | Material      |
|----------------------------|---------------|
|                            | RPC          | RPC Char     |
| Moisture                   | 6.6          | -            |
| Volatiles                  | 66.5         | -            |
| Fixed carbon               | 18.6         | 74.0         |
| Ash                        | 8.0          | 26.0         |

Chemical composition (dry and ash free wt.%)

|   | C     |   |  H    |   | N     |   | S     |   | O a   |   | HHV (MJ/kg) |
|---|-------|---|-------|---|-------|---|-------|---|-------|---|--------------|
|   | 45.9  |   | 6.8   |   | 5.8   |   | 0.4   |   | 41.1  |   | 19.1         |
|   | 57.3  |   | 0.6   |   | 4.5   |   | 0.1   |   | 37.5  |   | 17.3         |

a By difference.

Figure 1. Influence of particle size and temperature on the rate of RPC char gasification in the Ar/CO₂ mixture.

The results of the char characteristics of RPC are shown in Table 2. The yield of RPC char production during pyrolysis was equal to 25.4–25.9 wt.% of the initial sample mass.

The rates of RPC char gasification were measured under isothermal conditions at temperatures of 800, 850, and 900 °C. Two concentrations of carbon dioxide (10 and 50 mol. %) in the mixture with argon and pure CO₂ were used as gasifying media. In each experiment performed under atmospheric pressure, approximately 20 mg samples were heated in an inert atmosphere of Ar at 20 °C/min. Once the desired temperature was attained, the correct gas composition was set. The feed gas composition and total flow rate of 50 cm³/min were adjusted by mass flow controllers.

4. Results

4.1. Pyrolysis of RPC

RPC, similar to other types of plant biomass, is composed of cellulose, hemicellulose, lignin, and smaller amounts of other organic compounds, but the content of individual components can vary with the rapeseeds originating from different plantations. In addition, RPC contains a certain amount of unpressed oil, as well as moisture and 5–11 wt.% of nonvolatile mineral substances [7,8,23]. Useful information about the composition of biomass and its thermal characteristics is provided for thermogravimetric analysis.
The TG profile for the pyrolysis of the RPC sample in an inert argon atmosphere at a sample heating rate of 10 °C/min are shown in Figure 2. The DTG data (Figure 3) show that the thermal decomposition of RPC can be divided into several weight loss stages occurring at different temperatures.

![TG and DTG curves](image)

**Figure 2.** TG and DTG curves corresponding to the pyrolysis of RPC.

![Peak deconvolution](image)

**Figure 3.** Peak deconvolution of the DTG curve at 10 °C/min.

The total main weight loss of rapeseed oil cake was determined to be 70% at temperatures up to 600 °C, and there was only a slight weight loss (∼5 wt.%) in the high temperature range (600–1000 °C) due to evaporation and thermal cracking of the higher-molecular-weight primary pyrolysis products filling pores of the solid residue [24].

To elucidate the process mechanism, a deconvolution of the DTG curve into individual peaks was performed using the NETZSCH Peak Separation software, and the results are shown in Figure 3. The experimental data were fitted as an additive superposition of peaks, where each single peak was represented by the Fraser–Suzuki profile. The best fit to the DTG curve was achieved for a system consisting of six peaks. The correlation coefficient was 0.999. The peak position and the area fraction expressing a percentage of total mass loss of RPC in each single stage are given in Table 3.

### Table 3. Deconvolution peak characteristics.

| Peak No. | I  | II | III | IV | V  | VI |
|----------|----|----|-----|----|----|----|
| $T_{\text{max}}, ^\circ\text{C}$ | 77 | 229| 318 | 380| 442| 992|
| Temp. range, °C | 30–161 | 175–304 | 252–373 | 343–437 | 411–563 | 701–1000 |
| Area fraction, % | 6.9 | 19.5 | 33.7 | 20.3 | 8.0 | 11.6 |
In the first stage, the moisture adsorbed on the char was evaporated at temperatures below 200 °C. A major sample weight loss occurred between 170–600 °C due to thermal degradation of the carbohydrates, mainly hemicellulose cellulose and lignin components (peaks II, III, V). Similar results were reported in a previous study related to TG analysis of the pyrolysis of RPC [5,7]. According to the literature, the second peak, exhibiting a maximum at approximately 229 °C on the DTG curve as a shoulder of the peak with a maximum at 318 °C, should be attributed to the thermal degradation of hemicellulose [25]. The third weight loss step, which occurred between 250 and 370 °C, could be related to the degradation of the rapeseed oil cake cellulose. Smets et al. [7] showed that the fourth peak, which reaches the maximum at 380 °C, can be identified as the volatilization of triglycerides and their partial decomposition to fatty acids. Lignin decomposed over a higher temperature range [25]; therefore, decomposition of this component could be represented by the weight loss peak V with the maximum at approximately 442 °C.

The solid residue remaining after pyrolysis consists mainly of the mineral fraction and the deposited carbon formed at the earlier stages of the process. The solid is porous, with the pores being partly filled with molten volatile primary decomposition products (high-molecular-weight hydrocarbons). The oxidation of fixed carbon and thermal cracking of the substances filling pores takes place at sufficiently high temperatures, and these processes range from 600 to 1000 °C. Peak VI represents the abovementioned processes.

4.2. Kinetics of Char Gasification

The TG curves obtained under isothermal CO₂ gasification experiments were converted to carbon conversion on an ash-free basis, defined as:

\[ X = \frac{m_0 - m}{m_0 - m_F} \]  

(3)

where \( m_0, m \) and \( m_F \) represent the weight, % or mg, related to the initial mass of the sample, a given moment and a final solid residue of the process, respectively [26,27].

The formula can be used with an assumption that the ash decomposition is negligible. The experimentally obtained conversions are shown in Figure 4. These results demonstrate the effects of the temperature and CO₂ concentration on the reaction times needed for complete gasification. The raw data are shown in the form of symbols, while the meaning of the lines is explained later in the text.

Figure 4 also presents a dependence of reactivity (conversion rate \( dX/dt \)) of RPC char in CO₂ gasification on conversion. A maximum appears on the reactivity curves at a conversion of approximately 30%–40%. From this result, it follows that for the correct kinetic interpretation of the experimental data, the rate equation of the RPM model should be applied, as mentioned in Section 2.

To estimate the model parameters, a two-step procedure was applied. In the first step, approximate values of unknown model parameters were estimated, and in the second step, their final values were determined using nonlinear regression by minimization sum of squares of residual, SSR (deviations predicted from empirical values of conversions). A range of conversions from 0.05 to 0.9 was used for the model evaluation due to the uncertainty of the data obtained in the initial and final stages of the experiments.

At the beginning of the process, the reaction rate constants \( k_s \) for different temperatures and CO₂ concentrations were calculated as the slopes of the plots (shown in Figure 5) obtained by linearization of the experimental data with the integral form of the RPM rate equation, \( \Phi \), given in Table 1. The symbols on the plots represent the experimental data from Figure 4, and the solid lines represent their linear fits, as calculated by regressions.
Figure 4. Effect of temperature and gasifying agent concentration on conversion (b,d,f) and RPC char reactivity in the CO$_2$ gasification reaction (a,c,e).

Figure 5. (a) Plots of the linearized experimental data with the random pore model (RPM) equation for RPC char gasification under conditions 50% CO$_2$; (b) 10%, 100% CO$_2$.

The structural parameter $\psi$ needed to calculate $\Phi$ in the RPM model can be estimated from the experimental conversion values where the reaction rate is the maximum $X_{\text{max}}$ [28]. However, as shown in Figure 4, the position depends on the temperature and CO$_2$ concentration. In such a situation,
a better approach to estimate the structural parameter seems to be a method used by Everson et al. [29], where $\psi$ was calculated by fitting Equation (4) to all experimental results:

$$\frac{t_X}{t_{0.9}} = \frac{\sqrt{1 - \psi \ln(1 - X)} - 1}{\sqrt{1 - \psi \ln(1 - 0.9)} - 1}$$

(4)

where $t_X$ and $t_{0.9}$ are the times after which the conversion reaches $X$ and 0.9, respectively. A comparison of the conversions calculated from Equation (4) and the experimental results is shown in Figure 6 for $\psi = 6.8$, which was determined to be the optimal value for this parameter.

![Figure 6. Determination of the structural parameter.](image)

Then, using the reaction rate constants calculated at different temperatures and CO₂ concentrations, the approximate values of the activation energy, the pre-exponential factor, and the reaction order were estimated and used as initial values in further calculations. The effect of temperature over the range 800 to 900 °C with three concentrations of CO₂, as shown in Figure 7a, and the effect of carbon dioxide concentration over the range 0.1 to 1.0 mole fraction for two extreme temperatures, as shown in Figure 7b, show very similar trends, which made it easier to determine the parameters.

![Figure 7. (a) Arrhenius plot and (b) auxiliary graph for determining reaction order for RPM char gasification (the meaning of the symbols is the same as in Figure 4).](image)

As mentioned earlier, in the second stage of kinetic model identification, the final values of the model parameters were determined using nonlinear regression of the experimental data with the model rate equations. The Arrhenius parameters, the reaction order with respect to the carbon dioxide...
mole fraction, and the structural parameter were estimated by minimizing the objective function of the following form:

$$SSR(A, E, n, \psi) = \sum_{i=1}^{M} \sum_{j=1}^{N} \left( X_{ij, exp} - X_{ij, cal} \right)^2$$

(5)

where $X_{ij, exp}$ and $X_{ij, cal}$ are the char conversions determined experimentally and calculated from the model equations given in Table 1, $M$ is the number of experimental runs, and $N$ is the number of experimental data points in each run (in this case, $M = 7$ and $N = 17$). The optimal values of the model parameters are given in Table 4, and some fit statistics are included in Table 5.

Table 4. Optimal values of kinetic parameters in the RPM model for CO$_2$ gasification of RPC char.

| $A$, s$^{-1}$ | $E$, kJ·mol$^{-1}$ | $n$, - | $\psi$, - | $SSR$, - |
|----------------|-------------------|------|------|--------|
| 5.20·10$^6$    | 222.1             | 0.571| 6.1  | 0.186  |

Table 5. Fit statistics and results.

| $T$, K | $y_{CO_2}$, vol.% | $k_2$ Initial, s$^{-1}$ | Coefficient of Determination, - | $k_2$ Final, s$^{-1}$ | MAE*, - |
|--------|-------------------|------------------------|-------------------------------|-----------------------|---------|
| 1173   | 0.5               | $4.47 \times 10^{-4}$   | 0.998                         | $4.50 \times 10^{-4}$ | 0.016   |
| 1123   | 0.5               | $1.59 \times 10^{-4}$   | 0.999                         | $1.63 \times 10^{-4}$ | 0.01    |
| 1073   | 0.5               | $4.85 \times 10^{-5}$   | 0.999                         | $5.38 \times 10^{-5}$ | 0.038   |
| 1173   | 1                 | $6.07 \times 10^{-4}$   | 0.995                         | $6.68 \times 10^{-4}$ | 0.017   |
| 1073   | 1                 | $8.02 \times 10^{-5}$   | 0.998                         | $8.00 \times 10^{-5}$ | 0.036   |
| 1173   | 0.1               | $1.79 \times 10^{-4}$   | 0.99                          | $1.79 \times 10^{-4}$ | 0.022   |
| 1073   | 0.1               | $2.25 \times 10^{-5}$   | 0.998                         | $2.15 \times 10^{-5}$ | 0.038   |

* mean absolute error.

The optimal value of 6.1 for the structural parameter found in this study is similar to the $\psi$ value of 6 reported for rice husk char obtained by Gao et al. [30], while it is considerably lower than the values of 16.9–42.6 reported for coconut-shell chars [31]. When the $\psi$ value is higher than 2, pore growth increases the surface area of the solid reactant and the reaction rate during the initial stage of gasification [32]. The lower values of rice husk chars indicate that the chars would undergo limited pore development in the gasification process [33]. The values for the reaction order with respect to the carbon dioxide mole fraction (0.57) and the activation energy (222.1 kJ/mol) are within the ranges published in the literature [19].

5. Conclusions

The carbon dioxide gasification reaction rate of char derived from rapeseed press cake—the solid remaining after pressing rapeseeds to extract the oil—was investigated experimentally using thermogravimetric analysis under the conditions typical for fluidized bed gasifiers, i.e., atmospheric pressure and temperatures between 800 and 900 °C. CO$_2$–argon mixtures of concentrations 10 to 50 (by volume) and pure CO$_2$ were used as gasifying agents.

The random pore model with the parameter characterizing the initial pore structure of the char was evaluated by a two-step procedure based on all the experimental results obtained at different temperatures and carbon dioxide concentrations. This model is able to accurately predict the carbon conversion of RPC char as gasification proceeds under the conditions applied in this study. The model also predicts well the influence of conversion on char reactivity. In practice, the rate equation developed on the basis of the RPM model allows for estimation of the gasification time for different operational conditions.
The results of kinetic analysis indicate that the chars would undergo limited pore development during gasification. The values for the reaction order with respect to CO\(_2\) and the activation energy are within the ranges published in the literature for other biomass fuels.

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**Nomenclature**

- \( A \) pre-exponential factor, \( s^{-1} \)
- \( E \) activation energy, \( \text{kJ mole}^{-1} \)
- \( k_s \) first order reaction rate constant, \( s^{-1} \)
- \( k \) reaction rate constant independent of \( \text{CO}_2 \) concentration, \( s^{-1} \)
- \( L_0 \) total pore length per unit volume, \( \text{m} \cdot \text{m}^{-3} \)
- \( m_0 \) initial weight of the sample during the reaction, \( \text{g} \)
- \( m \) final mass of the sample at the end of gasification, \( \text{g} \)
- \( m_f \) actual mass of the sample during the reaction, \( \text{g} \)
- \( n \) order of reaction,\(-\)
- \( R \) universal gas constant, \( \text{kJ mole}^{-1} \cdot \text{K}^{-1} \)
- \( r_s \) intrinsic reaction rate, \( s^{-1} \text{ or } m \cdot s^{-1} \)
- \( S_0 \) initial surface area, \( \text{m}^2 \cdot \text{m}^{-3} \)
- \( T \) temperature, \( \text{K} \)
- \( t \) time, \( \text{s} \)
- \( X \) conversion,\(-\)
- \( y_g \) concentration of \( \text{CO}_2 \) in the gas stream, mol. fraction

**Greek symbols**

- \( \varepsilon_0 \) initial porosity of solid (char)
- \( \psi \) structural parameter

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