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## Experimental and modelling analysis of char decomposition: experiences with real scale gasification systems

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### Abstract

The main issue to be faced when dealing with gasification processes is the removal of tars in order to obtain a good quality producer gas for later use, either as energy vector or for production of chemicals. Char has been observed to have a high potential for catalytic tar reduction, but the properties that promote this activity are still being investigated. An understanding of the mechanisms involved in the process of tar removal is needed, including the deactivation of the char as a catalyst and its degradation. This work addresses the process of thermal decomposition of char with different operating conditions and under inert atmosphere (N<sub>2</sub>), in order to determine the mass loss occurring under high temperature treatment. For this purpose, chars collected from local gasification plants have been used. Firstly, a complete characterization of the chars has been carried out to determine their composition, heating value and BET surface area. Secondly, thermogravimetric analyses have been used to calibrate a one-step kinetic model for describing the kinetics involved in the process of char thermal decomposition. The coupling of the kinetics with a CFD model allowed then to consider mass, heat, and momentum transfer phenomena, and to quantitatively estimate the decomposition in a fixed-bed test reactor. The model, whose results have been compared to reference experimental tests, predicts satisfactorily the thermal behavior of the char inside the reactor and its mass loss.

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### 1. Introduction

The interest in gasification and pyrolysis processes has recently grown. Many applications exist for the gas (syngas or producer gas) that can be obtained from the conversion of biomass. The syngas can be used for separate or combined heat and power generation, but also for the production of liquid fuels and

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chemicals. One of the main issues of gasification processes is the formation, together with the gas, of by-products such as fly ash, nitrogen and sulphur oxides, char, and tar. Tar removal, in particular, is a very critical and challenging aspect, since the condensation at low temperatures of these aromatic hydrocarbons may cause the clogging of downstream equipment. Several methods (mechanical, catalytic, and thermal methods [1]) are available for tar reduction in biomass producer gas. Catalysts for cracking of tar have been widely investigated, with Ni-based catalysts and dolomites being the most researched ones [2]. In recent years, also char has gained interest for its catalytic activity in tar removal. The fact that char is a by-product of the process of gasification, makes it an inexpensive and very attractive solution for gas filtering. In South-Tyrol region (Italy), more than 40 small-scale gasification plants are currently operating, producing 800-1500 tons of char per year. There is therefore a significant interest in valorizing this by-product that would be otherwise disposed off as a waste and with considerable costs [3]. Abu El-Rub et al. [4] studied the catalytic performance of char and compared it with that of other catalysts. Char resulted to have higher activity for conversion of naphthalene than catalysts typically used for the purpose, like dolomite or olivine. Klinghoffer et al. [5] tested the catalytic performance of char for hydrocarbon cracking reactions, concluding that higher surface area increases catalytic activity, although the presence of micro-pores can lead to diffusion limitations, thus decreasing the reaction rates. The aim of this study is to examine the properties of some char samples collected in existing commercial plants in South-Tyrol and to study the thermal degradation of char for future use as filtering medium in tar cracking applications.

## 2. Materials and methods

### 2.1. Char sampling and characterization

Char samples have been collected from local small-scale gasification plants based on commercial gasification systems that use different biomass feedstock (wood chips or pellets), and different reactor technologies (downdraft or rising co-current). These technologies, henceforth indicated as technology A, B, C, and D, have been assessed by Patuzzi et al. [3] within the GAST project (GASification experiences in South Tyrol: energy and environmental assessment). The elemental composition and heating value of the collected chars have also been measured in this previous work. Moreover, in order to complete the characterization of the samples, specific surface area, pore size, and pore distribution have been measured by using the BET (Brunauer-Emmett-Teller) method, based on nitrogen adsorption at 77 K, and the 3Flex Physisorption Analyzer (Micromeritics Co., USA). This characterization is useful for identifying which char samples are more suitable for use as tar cracking catalyzers and should therefore be further studied.

### 2.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) has been performed on char samples in order to investigate their thermal behavior and characterize their decomposition under thermal treatment at constant temperature or at constant heating rate. Thermogravimetric tests have been carried out by means of a simultaneous thermal analyzer (STA 449 F3, Netzsch) in inert atmosphere (N<sub>2</sub>). Tests at different constant heating rates have been performed. More specifically, heating rates of 10, 30, and 50 K/min have been chosen, and the samples have been heated until 1000 °C. In addition, tests at constant temperature have been performed on one specific type of char, the one showing the highest surface area among the considered chars. These analyses have been later used for the calibration of the developed kinetic model. For the tests at constant temperature, the char samples have been heated at a constant heating rate of 10 K/min, kept for one hour at the chosen plateau temperature of 600 °C or 700 °C, and then heated again at 10 K/min until 900 °C. These temperatures

have been chosen after analyzing the TG curves at constant heating rates, being the temperatures at which the higher rate of decomposition is achieved.

### 2.3. Thermal degradation tests

In a laboratory-scale tubular fixed-bed reactor, char samples have been subjected to thermal degradation tests. The tests have been performed at different temperatures (700 °C and 900 °C), introducing the reactor – charged with a char bed – into the already heated furnace. The reactor, continuously fluxed with a constant nitrogen flow of 0.2 l/min, was kept inside the furnace for one hour and then removed and cooled down to room temperature. The mass of the samples has been measured before and after each test, and the decomposition of the char has been determined in terms of residual mass as a percentage of the initial mass. Besides the measure of the mass loss, by means of a thermocouple placed inside the reactor at 6 cm from the bottom, the temperature of the char has been monitored and registered throughout the test.

### 2.4. Kinetic model

The results obtained from the thermogravimetric analysis have been used to model the decomposition of char and, in particular, to derive the kinetic parameters describing it. Thermal degradation is a very complex process, since it encompasses several physical and chemical mechanisms that are not easily analyzed and simulated. For the purpose of this work, a simple one-step kinetic model has been used to describe the degradation of the char, calibrating it by means of the rates of weight loss measured experimentally in the thermogravimetric analysis. The overall process has been assumed to be an irreversible first-order reaction, during which the char, subjected to high temperatures and to a constant flow of nitrogen, decomposes into volatiles and a solid residue. The reaction rate  $r$ , which expresses the velocity at which the reaction proceeds, or, equivalently, the decomposition rate of mass  $m$ , is expressed as  $r = K \cdot m$ , where  $K$  is the rate of reaction constant, which, according to Arrhenius law, can be expressed, for a first-order reaction, as a function of the absolute temperature  $T$ . More specifically:  $K = K_0 \exp(-E_a/RT)$ , where  $K_0$  is the pre-exponential factor, also called frequency factor,  $E_a$  is the activation energy, which is the minimum energy required to allow the reaction to proceed, and  $R$  is the universal gas constant. When considering the process of degradation of char, it has to be taken into account that char decomposes into a gaseous and into a solid phase. Hence, two distinct rates of reaction have to be included in the modelling; the reaction rate  $K_V$ , relative to the formation of the volatiles, and the reaction rate  $K_S$ , relative to the formation of the solid residue. Both reaction rates can be expressed by using the Arrhenius law, and each will be characterized by its own pre-exponential factor ( $K_{0,V}$  and  $K_{0,S}$ , respectively) and activation energy ( $E_{a,V}$  and  $E_{a,S}$ , respectively). By using the results from the thermogravimetric analysis describing the char mass loss as a function of time and temperature, a system of equations based on the amount of mass lost in time has been defined and solved in MATLAB for obtaining the relevant kinetic parameters.

### 2.5. CFD modelling

Given the kinetics of the process, in order to have an estimation of the degradation of char under different operating conditions, it is necessary to integrate the results of the kinetic study in a model comprising both chemical and physical processes involved in the thermal degradation of the char. For the purpose, a CFD model reproducing the fixed-bed reactor has been realized in ANSYS Fluent. Once defined the geometry and the boundary conditions, mass, momentum, and heat transfer equations are solved all over the volume of the char modelled within the reactor. The temperature profiles simulated in the char bed have then been transferred to the kinetic model and used for predicting the amount of char that has decomposed in the

process. The boundary conditions in the modelled reactor have been set according to the thermal degradation tests performed on char samples. In particular, the temperature of the external wall of the reactor has been set at 700 °C, 800 °C, 900 °C, and 1000 °C and a transient-time simulation has been performed with a time step of one second. For validating the model, the values of the char residual mass obtained experimentally from the thermal degradation tests have been compared with the results from the model. The modelling of the char mass loss occurring under a certain operating temperature and atmosphere would allow to understand if it is possible to design an autonomous gasification system in which self-produced char is sufficient to be effectively used for tar cracking and hence for cleaning of the producer gas.

### 3. Results and discussion

#### 3.1. Char characterization and thermal analysis

The data of the elemental composition, taken from [3], show that all the char samples under analysis have a negligible amount of nitrogen, ranging from 0.23% to 1.98%. On the other hand, the carbon content is quite high, ranging from 48.03% to 87.58%. The lowest value pertains to technology C, because of the high ash content of the produced char, that is 49.52%, much higher than the ash content found in the char produced from technologies A, B, and D, which ranges from 8.68% to 27.84%. The hydrogen and oxygen concentrations in the chars are in the range 0.33% - 0.98% and 0.78% - 2.37%, respectively. The elemental composition of the chars is reported in the Van Krevelen diagram in Figure 1a, in which the H/C ratio is plotted against the O/C ratio. For comparison, data found in literature [6] and relative to several solid fuels have been included in the diagram. The lower heating values of the chars and the specific surface area determined experimentally are also reported (Figure 1b). The char obtained from technology A shows the largest surface area, equal to 352.42 m<sup>2</sup>/g. Since many studies [4,5,7], have demonstrated that the higher the specific surface area, the higher the activity of a catalyst, this char is the most promising for tar cracking applications, and it has therefore been chosen for the calibration of the modelling presented in this study. Figure 2 shows the thermogravimetric curves (TGA and DTG) performed on char A at different heating rates (10, 30, and 50 K/min) in the temperature range 40 °C – 1000 °C. Since the DTG curves showed a peak of mass loss between 600 °C and 700 °C independently of the heating rate, additional TG analyses have been performed at a constant temperature of 600 °C and 700 °C, in order to have a smoother description of the degradation process and thus a better calibration of the kinetic model.

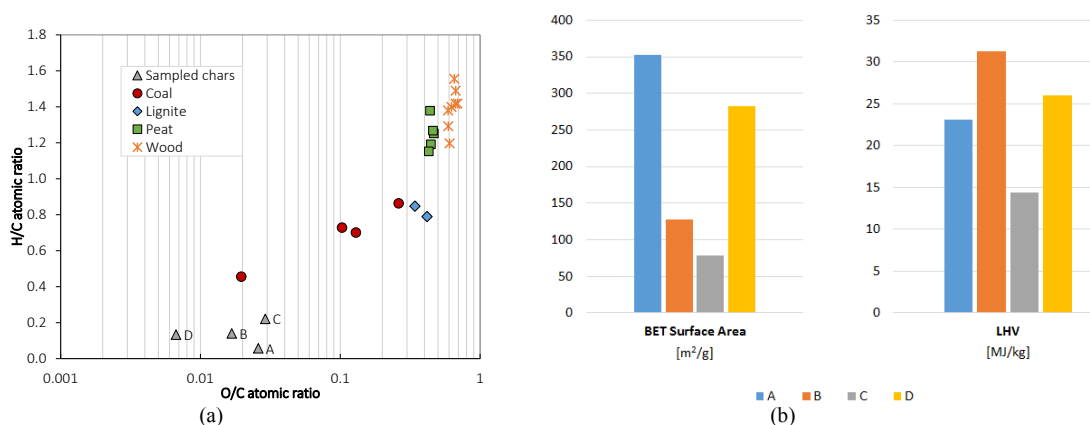


Figure 1. (a) Van Krevelen diagram; (b) BET surface area and lower heating value of sampled chars.

### 3.2. Kinetic model calibration

The TGA curves obtained for char A at constant temperature, have been used for solving the system of equations expressing the change of mass in time, and finding the kinetic describing the process of char degradation. The resulting values representing the two processes comprised in the decomposition of char, are  $K_{\theta} = 4.80 \text{ E-}04 \text{ s}^{-1}$  and  $E_a = 1.0 \text{ kJ/mol}$  as regards the formation of the solid residue, and  $K_{\theta,V} = 1.75 \text{ E-}03 \text{ s}^{-1}$  and  $E_{a,V} = 16.5 \text{ kJ/mol}$  as regards the formation of the volatiles. The TGA curves at constant temperature simulated by using these kinetic parameters are shown in Figure 3.

### 3.3. Thermal degradation tests and CFD model

The thermal degradation tests performed in the laboratory-scale fixed-bed reactor at 700 °C and 900 °C, gave, after one hour tests, a final residual mass of 94% and 86%, respectively. The CFD model has been used for simulating these tests and predict the residual mass by integrating the temperature results into the developed kinetic model. The simulations have been run also for predicting the residual mass at temperatures of 800 °C and 1000 °C. The results are reported in Table 2.

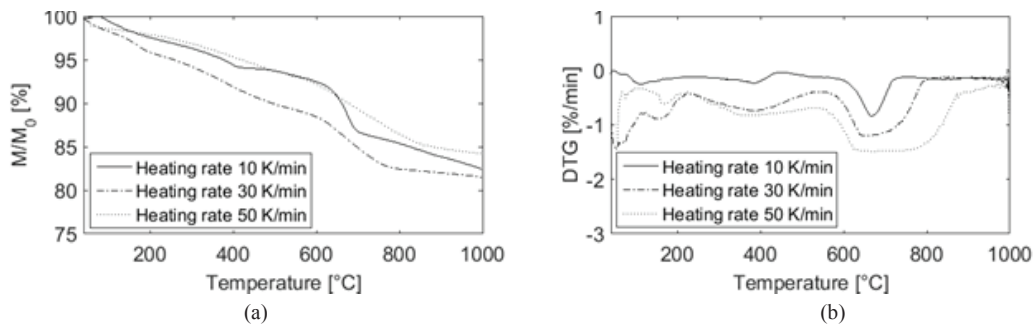


Figure 2. (a) Thermogravimetric curves of char A; (b) DTG curves of char A.

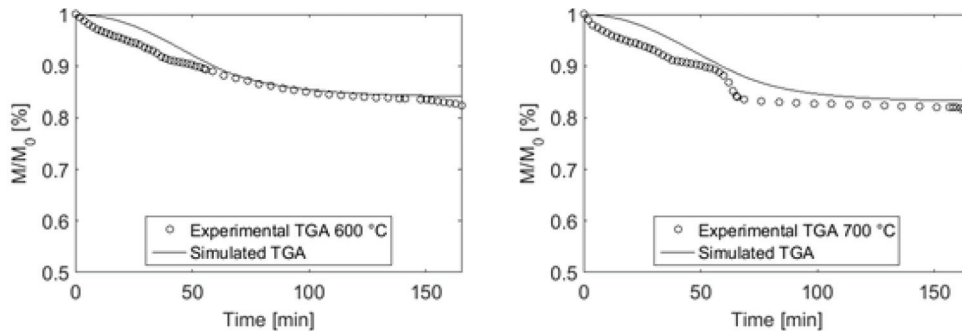


Figure 3. Experimental and simulated TGA curves at constant temperature.

Table 2. Residual mass after thermal degradation tests at different operating temperatures.

Temperature	Experimental residual mass	Residual mass from model
700 °C	94%	80.19%
800 °C	-	76.47%
900 °C	86%	73.07%
1000 °C	-	69.99%

#### 4. Conclusions

Char samples collected from small-scale gasification systems have been analyzed, and the char with the highest potential for catalytic activity (largest specific surface area) has been selected for modelling the process of degradation under high temperatures and inert atmosphere. The model predicts the thermal behavior of the char inside the reactor and its mass loss, complying satisfactorily with the experimental tests. This study represents a preliminary work for assessing the potential use of char as a catalytic gas filtering medium for gas cleaning applications. Further analyses (e.g. experimental tests with model tar compounds, study of the deactivation of char as catalyst) are needed in order to investigate the char catalytic activity on the removal of tar from the producer gas, and design a gasification system supported by use of the char that is self-produced during the gasification process.

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Francesco Patuzzi received his PhD in 2014 and is presently assistant professor at the Faculty of Science and Technology at the Free University of Bozen-Bolzano (Italy). His research activities are mainly related to the study of thermochemical conversion of ligno-cellulosic biomasses, with a particular focus on the process by-products valorization.