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Gasification Studies on Argentine Solid Fuels

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1. Introduction

As the global population growth and energy demand are steadily raising and the industry is forced to reduce the greenhouse gas emissions due to the global warming, there is an increasing pressure to improve the overall efficiency of the energy production systems. In this challenging framework, a renewed interest on coal gasification technologies has recently emerged worldwide, since they offer the potential of clean and efficient energy. One attractive characteristic of coal gasification technology is the possibility of co-production of electricity, hydrogen, liquid fuels and high-value chemicals that contributes to the improvement of power generation efficiency compared with conventional pulverised coal fired plants as well as the reduction of emissions of greenhouse gases and particulates to the atmosphere (Minchener, 2005). Gasification has also the additional advantage of accommodating a wide range of feed stocks, including low-cost fuels like petroleum coke, biomass, and municipal wastes (Higman & Van der Burgt, 2003).

As it will be explained in Section 2, Argentina is presently investigating the application of the concept of co-production for the integral exploitation of its coal reserves. Co-production of power, fuels and chemicals offers an innovative, economically advantageous mean of achieving the long-term energy goals of our country since it involves the integration in a single energy complex of three major building blocks: (1) gasification of coal to produce synthesis gas; (2) conversion of a portion of the synthesis gas to high-value products, such as high-purity hydrogen and liquid fuels; and (3) combustion of the remaining synthesis gas and unreacted gas from the conversion processes to produce electric power in a combined-cycle system. In the co-production concept, an energy complex produces not only power, but also fuels and/or chemicals. This concept greatly increases the flexibility of the complex and offers economic advantages compared with separate plants, one producing only power and the other only fuels or chemicals.

Following this objective, an extensive research and development program is being implemented in our country on solid fuel gasification technologies, beginning with both

theoretical and experimental studies for understanding the mechanisms of the gasification reactions, in order to determine the optimum parameter conditions for the synthesis gas production and the further cleanup steps for the harmful contaminants removal. For providing indirect heating to the gasification reactors, replacing the partial combustion of the feed material that is needed to drive the endothermic gasification reactions, the alternative of using a nuclear high temperature gas reactor is being also evaluated (Nassini et al., 2011).

It is well-known that the chemical composition, the heating value and, then, the future use of the synthesis gas produced by solid fuel gasification is variable with the gasification technology employed, depending on a lot of factors such as solid fuel composition and rank; pre-processing and feeding procedures; gasification agents; operational conditions in the gasification reactor, i.e. temperature, pressure, heating rate, and residence time; and plant configuration characteristics like the flow geometry, ash removal method and gas cleaning system. There is a large number of gasification processes implemented at commercial level and the choice of a given gasification technology is difficult because it depends on diverse factors such as solid fuel availability, type and cost; size constraints; and production rate of energy. Even, in principle, all types of solid fuels can be gasified, the properties of the material to be processed are the least flexible factor to be considered in the analysis and, then, the gasification technology should be primarily matched to the properties of the solid fuels available for gasification (Collot, 2006).

According to that, a theoretical and experimental study is being now performed at laboratory scale, addressed to characterize the behaviour of Argentine solid fuels under typical gasification conditions and to identify the most suitable gasification process for the production of hydrogen and liquid fuels, respectively. The research program that is described below was designed to simulate in laboratory, as close as possible, the operational conditions of large-scale gasification plants and to provide the necessary information about fundamental mechanisms and kinetics of the gasification reactions for a further scaling up of experimental facilities.

2. Argentine energy situation and scientific background

The current energy matrix of Argentina is largely based on fossil fuels, i.e. petroleum oil and natural gas, but the preservation of non-renewable resources and the minimization of pollution are goals which today determine decisively further development of fossil fuel-fired power stations. In this sense, a so-called Hydrogen Law was dictated by the Argentine Congress in 2006 declaring of national interest the development of technologies needed for the progressive introduction of hydrogen as a clean energy carrier that can be used to meet the increasing residential, transportation and industrial demands. According to that, the national government is promoting all scientific activities related with the production, purification, safe storage and applications of hydrogen, as well as the development of more efficient energy production systems (Bohe & Nassini, 2011).

In order to bring together the requirements of a sustainable economic growth with the environmental protection, our country is then encouraging strategies for the rational and integral utilization of domestic coal reserves and this tendency is expected to increase with time, as natural gas and petroleum resources are becoming exhausted. The main domestic coal reserve accounting more than 7% of conventional energy resources of Argentina is a high-volatile sub bituminous coal that is extracted from the Río Turbio minefield, located in Santa Cruz province, in the south of the country (Carrizo, 2002). Another materials containing carbon and amenable to be gasified are asphaltites arising from minefields located in Mendoza (Beloff, 1972) and Neuquen (Savelev et al, 2008). Asphaltites would be an excellent raw material for the production of synthesis gas through solid fuel gasification due to their low content of ashes and high percentage of elemental carbon (Fouga et al., 2011).

It is well-understood that solid fuel gasification is a two-step process. In the first step, pyrolysis, volatile components of feed material are rapidly released at temperatures between 300 and 500 ºC, leaving residual char and mineral matter as by-products. The second step, char conversion, involves the gasification of residual char and it is much slower than devolatilization step, becoming then the rate-limiting step of the overall process. Even gasification reactions have been extensively studied during years worldwide, a better understanding of the fundamental reaction mechanisms and kinetics is still required for optimizing the design and operation of large-scale gasifiers in order to maximize the efficiency and economics of the overall gasification process.

Earlier studies demonstrated that the reactivity of chars to gasifying agents is very dependent on their formation conditions, particularly temperature, pressure, heating rate, time at peak temperature, and the gaseous environment. When volatile matter is generated, the physical structure of char changes significantly and swelling of fuel particles may occur. The complexity of char structure lies in the facts that the structure of a char itself is highly heterogeneous inside an individual particle and between different particles and the chemistry of a char is strongly dependent on the raw material properties. Then, a good understanding of the swelling of particles and the formation of the char pore structure during the devolatilization step, as well as the further evolution of the released volatile matter is essential to the development of advanced gasification technologies (Yu et al., 2007).

On the other hand, even coal is generally classified by its rank with fixed carbon content and calorific value as the major indicators, coal rank related parameters do not always provide adequate predictors for gasification reactivity since coals of similar rank may undergo quite different extents of reaction when they are gasified at a particular condition. Additionally to coal rank, reaction conditions and sample preparation procedures, several other factors are thought to influence the coal gasification reactivity such as the mineral matter content of coals which is known to influence the gasification reactivity because of the presence of reportedly catalytically active components (Domazetis et al., 2005).

3. Experimental approach

When introduced into a high-temperature atmosphere in a gasification reactor, solid fuel particles are heated at high heating rates (above 10^3 ºC/sec) and they undergo devolatilization and gasification simultaneously under more or less the same condition. In spite of this evidence, most of the char reactivity data reported in literature was obtained under gasification conditions that were different from the devolatilization conditions under which the chars were prepared. According to that, a high spread in char reactivity measurements is found, even for chars prepared from the same parent coal but under different pyrolysis conditions (Peng et al., 1995).

As earlier studies have demonstrated that the reactivity of chars to gasifying agents is very dependent on their formation conditions, to get meaningful data about kinetics of gasification reactions it is essential, at least, to produce chars in laboratory that replicate, as close as possible, the real conditions of char formation in large-scale gasifiers, i.e. high heating rates and intense gas convection around individual char particles.

The experimental approach followed to achieve both objectives in the char preparation is the so-called "two-stage" experiments in which the gasification reactivities are determined on char samples prepared in a previous pyrolysis step where parent coal particles are heated in an inert atmosphere at high heating rates and short residence times at high temperatures (Megaritis et al., 1998). A drop tube furnace was designed and built up for producing chars in laboratory at temperatures up to 1100 ºC and heating rates in the order of 10^3 ºC/sec, while the CO_2 and steam gasification reactivities of these ex-situ chars were measured in a thermo-gravimetric system adapted to work with corrosive gases and in tubular reactors coupled with gas chromatography. The experimental setups used for pyrolysis and gasification experiments are described in more detail in the following section.

4. Experimental procedures and methods

4.1. Characterization of solid fuels for gasification experiments

The first step of the experimental program consisted of a detailed physical and chemical characterization of the Río Turbio coal and several asphaltites called Emanuel, Susanita, Fortuna 4 and Toribia, and the main results are summarized in Table 1. It can be seen that Toribia and Fortuna 4 asphaltites have the highest volatile content (above 50 wt%) while Emanuel asphaltite has the highest fixed carbon content. Furthermore, the Río Turbio coal has the greatest ash content and porosity. BET areas were measured by N_2 adsorption/desorption according to Barrett–Joyner–Halenda (BJH) method (Barrett, 1951), and using Digisorb 2600 equipment (Micrometrics Ins. Corporation). The analysis of elemental composition indicates the presence of nickel and vanadium in three of the asphaltites, and the recovery of theses valuable metals could be of economical interest. Calcium and sodium, silicon and iron are present in most of the samples. The XRD measurements indicate that those elements are forming the following majority phases: quartz, calcium sulfate, hematite, and aluminum silicates.

Determination	Solid Fuels				
	Coal	Asphaltites			
	Río Turbio	Emanuel	Susanita	Fortuna 4	Toribia
Moisture	3.5 (wt %)	11.47 (wt %)	10.93 (wt %)	0.26 (wt %)	0.58 (wt %)
Volatile matter[a]	36.4 (wt %)	26.18 (wt %)	33.18 (wt %)	58.97 (wt %)	56.06 (wt %)
Fixed carbon[a]	51.2 (wt %)	68.67 (wt %)	55.50 (wt %)	40.57 (wt %)	43.25 (wt %)
Ash[a]	12.3 (wt %)	5.13 (wt %)	11.32 (wt %)	0.46 (wt %)	0.69 (wt %)
Density	1.107 (g·cm³)	0.679 (g·cm³)	0.642 (g·cm³)	0.412 (g·cm³)	0.427 (g·cm³)
C_T	59.8	64.3	63.6	78.0	75.3
N_T	2.78	3.27	3.24	2.92	3.14
S_T	0.86	2.36	0.7	4.5	4.40
Determination	**Char**				
BET area	96 (m²·g⁻¹)	3.5 (m²·g⁻¹)	3.17 (m²g⁻¹)	0.44 (m²·g⁻¹)	na
Pore volume	0.064319	0.01495 (cm³g⁻¹)	na	na	na
Total porosity, ε_0	12 %	1.6 %	na	na	na
Ash content	20 %	6.95 %	16.94 %	1.12 %	1.57 %
Determination	**Ash**				
Elements present in Ash[b]	Na, Mg, Al, Si, K, S, Ca, Ti, Fe.	S, Ca, V, Fe, Si, Al, Ba, Ni, K, Sr, Mo, P, Cu.	Mg, Al, Si, S, Ca, V, Fe, Ni, Zn.	Na, Mg, Al, Si, K, Ca, V, Fe, Ni, Cu.	Na, Al, Si, K, Ca, V, Fe, Ni.
Main phases in Ash[c]	Fe_2O_3, SiO_2	SiO_2; Fe_2O_3; $CaSO_4$; $Ca_3V_2O_8$; $CaSiO_3$; $(Na,Ca)Al(Si,Al)_3O_8$	$CaSO_4$; SiO_2; $Ca_2Al_2SiO_7$.	SiO_2; NaV_6O_{15}	SiO_2; CaV_2O_6; $Al_6Si_2O_{13}$

[a] Moisture free

[b] Energy dispersive spectroscopy (EDS) and Energy dispersive X-Ray fluorescence spectroscopy (ED-XRF).

[c] X-Ray diffraction (XRD).

[na] not available

Table 1. Physical and chemical characterization of the Río Turbio coal and asphaltites.

4.2. Drop tube furnace for pyrolysis experiments

The drop tube furnace (DTF) that is shown in Figure 1 was used for preparing chars at high heating rates and short residence times at high temperatures from the Río Turbio coal and asphaltites. The reactor has a three-zone electric furnace able to operate up to 1100 ºC, which surrounds two concentric quartz tubes of 41 and 26 mm inner diameter, 1.30 and 1.20 m long, respectively. Primary nitrogen gas is injected at the bottom of the outer tube and is preheated while flowing upwards. When at the top of the outer tube, the gas is forced onto the inner tube through a flow rectifier and the gas flows downwards and leaves the reactor through a water-cooled collection probe. The solid fuel particles are entrained by a non-preheated secondary nitrogen gas jet to a water-cooled injection probe placed on top of the inner tube. The heating rate is estimated to be higher than 10^3 ºC/sec and the residence time

of particles in the reactor less than 0.3 sec. The chars leave the reactor through the collection probe, and an extra nitrogen flow is added to the exhausted gases in order to quench the reaction and improve the collection efficiency in the cyclone.

The major operating parameters in the reactor were: (1) temperature of pyrolysis, ranging between 700 to 1100 ºC; (2) mass flow of solid fuel particles, through variations in the secondary nitrogen gas flow; and (3) particle residence time at high temperature, derived from the heated tube length which can be varied since the three axial zones have independent electric power supply.
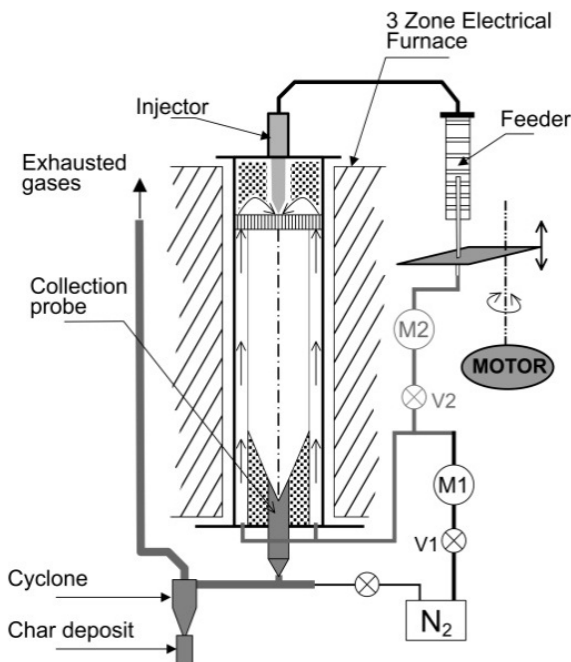
Figure 1. Drop tube furnace for pyrolysis experiments: (a) schematic view; (b) photograph taken during assembly.

4.3. Thermo-gravimetric system for gasification experiments

Gasification experiments using carbon dioxide and steam as gasifying agents were carried out in a thermo-gravimetric analyzer (TGA) that is schematically shown in Figure 2. This experimental setup consists of an electro-balance (Model 2000, Cahn Instruments, Inc.), a gas line, and a data acquisition system, having a sensitivity of ± 5 μg while operating at 950 ºC under a flow of 8 L/h. In a typical TGA run, the weight of the char sample is measured as a function of time and temperature as it is subjected to a controlled temperature program. TGA tests are usually carried out in two ways: (i) isothermal, where the sample is heated at a constant temperature, and (ii) non-isothermal with linear heating, where the sample is heated at a constant temperature rate.
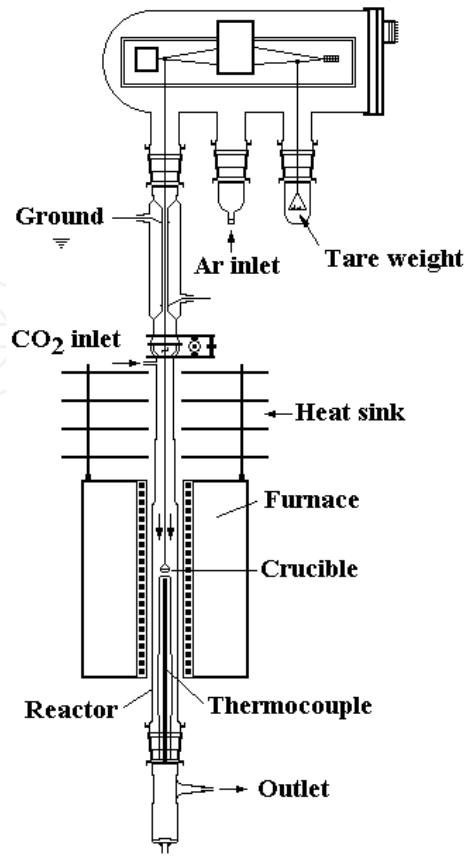
Figure 2. Thermo-gravimetric system for gasification experiments with carbon dioxide and steam.

The gasification rate under several experimental conditions of temperature, partial pressure of gasifying agent and sample mass, can be obtained from the temporal evolution of relative mass loss of char, as follows:

$$\alpha = \frac{m_0 - m}{m_0 - m_{ash}} \tag{1}$$

where m_0 is the initial mass of char, m is the mass of char at time t, and m_{ash} is the mass at the end of the gasification reaction when there is no more fixed carbon and corresponds to the ash content. According to equation (1) α takes values in the range between 0 and 1 and, hence, the gasification rate, R, can be expressed as:

$$R = \frac{d\alpha}{dt} = -\frac{1}{(m_0 - m_{ash})} \frac{dm}{dt} \tag{2}$$

In mathematical form, R is expressed as a function of temperature (T), partial pressure of gas (p_{gas}) and reaction degree (α), as follows:

$$R = \frac{d\alpha}{dt} = K(T)F(p_{gas})G(\alpha) \tag{3}$$

where K(T) refers to an Arrhenius type equation, F(p_{gas}) expresses the dependence of R with the partial pressure of gasifying agent, and G(α) is a function that describes the geometric evolution of the reacting solid. This procedure allows to exclude mass sample effects and represents an appropriate approach for the analysis of gas-solid heterogeneous reactions (De Micco et al., 2010).

4.4. Tubular reactors coupled with gas chromatography

Gasification experiments using carbon dioxide and steam as gasifying agents were also carried out in tubular reactors coupled with gas chromatography. The experimental setup for gasification experiments with carbon dioxide is shown in Figure 3 and consists of a horizontal quartz tube surrounded by an electrical furnace, a gas control panel, and a gas chromatograph (SRI 8610 C) with a packed column Alltech CTR I and helium as carrier gas. Solid char samples of 10 mg were placed on a flat quartz crucible forming a loose packed bed and inside the tubular reactor where an argon flow of 3.5 L/h was maintained. For the isothermal experiments, char samples were heated at the working temperature for about 1 hour after which carbon dioxide was introduced into the reactor. At the same time, the exhausted gases were injected in a gas chromatograph every 5 minutes. To inject the gases into the chromatograph, the exhausted gas stream was connected to a 1 ml loop and, according to the gaseous flow used, the time required to fill the loop was 0.86 seconds. The Reynolds number corresponding to the experimental conditions indicates that the gaseous flow inside the reactor is laminar (De Micco et al., 2012).
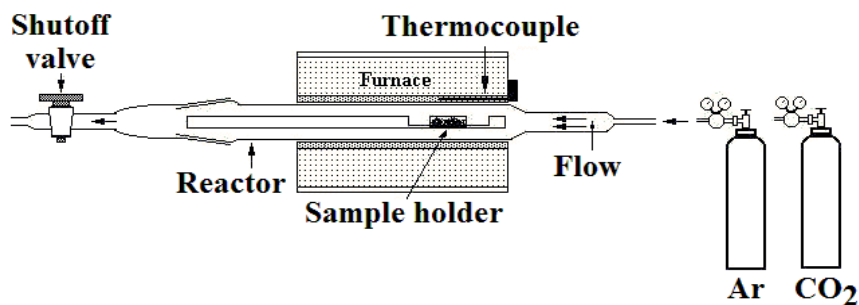

Figure 3. Tubular reactor coupled with gas chromatography for CO$_2$ gasification experiments.

The gasification rate is determined by monitoring the evolution of the concentration of reaction product, i.e. carbon monoxide (CO(g)), as a function of time. To follow the gasification kinetics, the peak areas corresponding to CO(g) concentration from the chromatograms registered every 5 minutes during the reactions are used. These areas are proportional to the amount of CO(g) moles formed during the time interval required to fill the loop. Since this time interval of 0.86 s is very small compared to the total time needed to achieve the complete reaction (more than 3000 sec), and assuming that no significant axial mixing occurs under laminar flow conditions, it can be considered that the peak areas are proportional to the instantaneous gasification rate. Plots of *CO-Area vs. time* were constructed for each gasification reaction and these experimental data were fitted with appropriated curves.

The number of moles formed at the time t can be calculated by integrating the curves from $t = 0$ to t, and the degree of reaction at time t can be obtained from the ratio of the previous result and the value of integrating the whole *CO-Area* vs. *time* for the complete gasification reaction, according to the following equation:

$$X(t) = \frac{n_{CO}(t)}{n_{CO}(t_f)}$$
(4)

where *X(t)* is the degree of reaction at time *t*, $n_{CO}(t)$ is the number of moles of CO(g) formed from the beginning of reaction until time *t*, and $n_{CO}(t_f)$ is the total number of moles of CO(g) formed during the whole reaction.

The experimental setup for gasification experiments with steam is shown in Figure 4 and consists of a horizontal quartz tube surrounded by an electrical furnace, a gas control panel, a steam generator, a set of thermal and chemical traps for retaining the water molecules from the gaseous stream, and a gas chromatograph for analysing the gasification products. The kinetics of gasification reactions can be followed either by measuring the concentration of reaction products with the chromatograph or by gravimetric measurements in which case the gasification reaction is stopped at different reaction degrees.
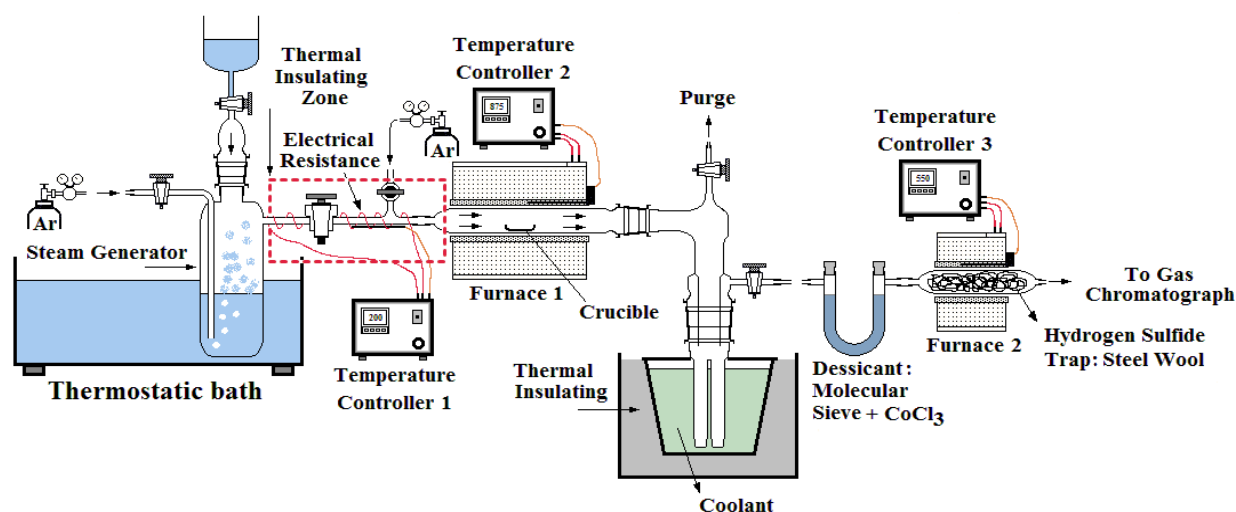

Figure 4. Experimental setup for gasification experiments with steam.

5. Modelling of gasification reactions

A good understanding of solid fuel reactivity and reaction kinetics with carbon dioxide and steam is required for careful optimization of gasification processes. For this reason, numerous studies are being performed worldwide in order to determine the kinetic parameters and reaction mechanisms of the gasification reactions, for each type of parent coal and char. In general, the gasification reaction is a heterogeneous gas-solid reaction where a porous solid is consumed leading to the formation of gaseous products such as carbon dioxide, carbon monoxide and hydrogen, and ash as a solid residue.

In order to obtain the kinetic parameters of gasification reactions, it is useful to measure the reaction rate under chemical control regime. To do that, it is necessary to find the experimental conditions under which mass-transfer resistance is absent. This is accomplished by changing the experimental parameters that influence the rate of the mass transfer processes occurring during the reaction.

Three main kinds of mass transport processes involving different physical phenomenon can be distinguished in this type of reaction: (a) transport of the gaseous reactant by bulk motion (mass convection); (b) transport of the gaseous reactant and products through the gaseous boundary layer (mass gaseous diffusion); and (c) transport of gaseous reactant and products within the solid pores (ordinary or Knudsen gaseous diffusion). The experimental parameters that can be systematically modified in order to make the mass transfer rate faster than the chemical reaction rate are the gaseous flow rate and the initial amount of solid reactant. Once the conditions are achieved to measure the reaction rate under chemical control in the selected range of temperatures, it is possible to apply different reaction models for describing the solid evolution during the reaction, and for obtaining the mathematical expression for the reaction rate.

In general, porosity, surface area and particle size of the solid fuel may vary during the reaction. There are many models that consider the effect of these changes to a different extent and, depending on the hypotheses the models can face various degrees of complexity. Furthermore, due to the porous nature of coal and char, it is not always possible to achieve complete chemical control of the reaction because the diffusion within the pores limits the overall rate of reaction. When this happens, both processes, chemical reaction and pore diffusion, exert an influence on the progress of reaction. Consequently, it is necessary to take into account mass transfer effects in the reaction rate expression.

Many models were developed and published for modeling the coal gasification reactions since the 1950s up to now. One of first approaches was done by Pettersen (Pettersen, 1957) who presented a method for a linear kinetic expression in the concentration and where appreciable concentration gradients were established in the pore system. He assumed uniform cylindrical pores with random intersections. The grain model was further developed by Szekely et al. (Szekely et al, 1976), representing the diffuse reaction zone of reacting porous solids and considering a solid made up of individual grains of equal size which could be spheres, long cylinders or flat plates. In this model, the solid surface area decreases nonlinearly with increasing the reaction degree. On the other hand, Bhatia & Perlmutter (Bhatia & Perlmutter, 1980) presented the random pore model which allows for arbitrary pore size distributions. In this model, the reaction surface changes due to two competing processes: (1) the effect of pore growth during gasification; and (2) the destruction of pores due to coalescence of neighboring pores. The model subsumes several earlier treatments as special cases. Other published models are the random capillary model (Gavalas, 1980), the discrete random pore model (Bhatia & Vartak, 1996), and the modified discrete random pore model (Srinivasalu et al., 2000).

In the analysis of gasification experiments with Argentine solid fuels, two different models were applied: (1) the grain model; and (2) the random pore model, and the mathematical formalisms are described briefly below.

Assuming separation of variables, the kinetic expression for the reaction rate is given by:

$$\frac{dX}{dt} = k(T)G(C_g)f(X) \tag{5}$$

being $X(t)$ the degree of reaction; $k(T)$ and $G(C_g)$ include the effects of temperature and gaseous reactant concentration in the reaction rate, respectively; and $f(X)$ accounts for the changes in physical or chemical properties of reacting solid with reaction degree.

The temperature dependence, i.e. the apparent reaction constant $k(T)$, is given by an Arrhenius equation with k_0 being the pre-exponential factor and E_a the activation energy. The gas concentration dependence, $G(C_g)$, is given by a power law expression being n the reaction order with respect to gaseous reactant concentration, resulting :

$$k(T)G(C_g) = k_0 e^{-E_a/RT} C_g^n \tag{6}$$

Replacing $f(X)$ by the grain model for spherical grains (GM) and the random pore model (RPM) the expressions for the reaction rate and reaction degree vs. time are the following:

- Grain model:

$$\frac{dX}{dt} = k_0 e^{-\frac{E_a}{RT}} \left(1-X\right)^{\frac{2}{3}} \tag{7}$$

$$3\left[1-\left(1-X\right)^{1/3}\right] = k_{GM}t \tag{8}$$

- Random pore model:

$$\frac{dX}{dt} = k_0 e^{-\frac{E_a}{RT}} \left(1-X\right)\sqrt{\left[1-\psi\ln\left(1-X\right)\right]} \tag{9}$$

$$\left(2/\psi\right)\left[\sqrt{\left(1-\psi\ln\left(1-X\right)\right)}-1\right] = k_{RPM}t \tag{10}$$

In the random pore model, in addition to the apparent reaction constant k_{RPM} there is another parameter, Ψ, which is related with the pore structure of the initial sample, and can be calculated from the experimental results with the following equation:
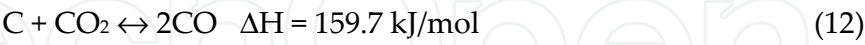
$$\psi = \frac{2}{2\ln\left(1-X_{max}\right)+1} \tag{11}$$

where X_{max} is the value of reaction degree where the reaction rate is maximum.

6. Main results and discussion

6.1. Experimental design

Laboratory research activities on gasification reactions of Argentine solid fuels in presence of carbon dioxide and steam comprised a comprehensive theoretical and experimental study on the following two chemical reactions:

$$C + CO_2 \leftrightarrow 2CO \quad \Delta H = 159.7 \text{ kJ/mol} \qquad (12)$$

$$C + H_2O \leftrightarrow CO + H_2 \quad \Delta H = 118.9 \text{ kJ/mol} \qquad (13)$$

After determining the experimental conditions to get the chemical control regime of gasification reactions in the different experimental setups through the variation of the gaseous flow, sample mass and char particle size, which are detailed in Table 2, the effects of the following parameters were investigated:

1. Composition and rank of feed material, i.e. comparative behaviour of subbituminous coal and asphaltites;
2. Reaction temperature, in the range between 800 and 950 ºC;
3. Partial pressure of gasifying agent, between 30 and 80 %v/v;
4. Conditions of char formation, using chars prepared in the DTF at 850 and 950 ºC, respectively, and chars prepared in a fixed bed reactor at 950 ºC.

Gasifying agent	Río Turbio Coal		Emanuel Asphaltite	
	TG system	GC system	TG system	GC system
CO_2	Gaseous flow above 7.3 L/h. Sample mass below 10 mg.	Gaseous flow above 4.2 L/h. Sample mass below 16 mg.	Gaseous flow above 5 L/h. Sample mass below 2.5 mg.	na
H_2O	na	na	na	Gaseous flow above 2 L/h. Sample mass below 25 mg.

Table 2. Experimental conditions to get chemical regime in gasification reactions.

The main results of the theoretical and experimental research program are given in the following sections.

6.2. Effect of solid fuel composition and rank

Argentine solid fuels were pyrolysed in inert atmosphere (argon) using non-isothermal TGA runs and the resulting TGA curves are presented in Figure 5. The mass losses observed in all cases are due to a mixture of vapors and gases which are released during heating, including CO_2, CO, hydrocarbon species, tars, and so on, and they are in agreement with the corresponding values of volatile matter content given in Table 1.

Figure 5 shows that Fortuna 4 and Toribia asphaltites behaved similarly during pyrolysis, exhibiting a fast volatilization rate between 300 and 500 ºC where about 70 wt% of the total volatile matter was released, replicating the results of the proximate analyses where both materials showed very similar values of fixed carbon, ash and volatile matter. The same agreement between proximate analyses and non-isothermal TGA curves was detected for Susanita asphaltite and Río Turbio coal; in this case, two different portions can be distinguished in TGA curves: (1) a fast volatilization rate between 300 and 500 ºC where about 60 wt% of the volatile matter was released, and (2) a slow volatilization rate above 500 ºC where about 25 wt% of the volatile matter was further released. Finally, Emanuel asphaltite showed a singular behavior with a nearly constant volatilization rate between 300 and 900 ºC.
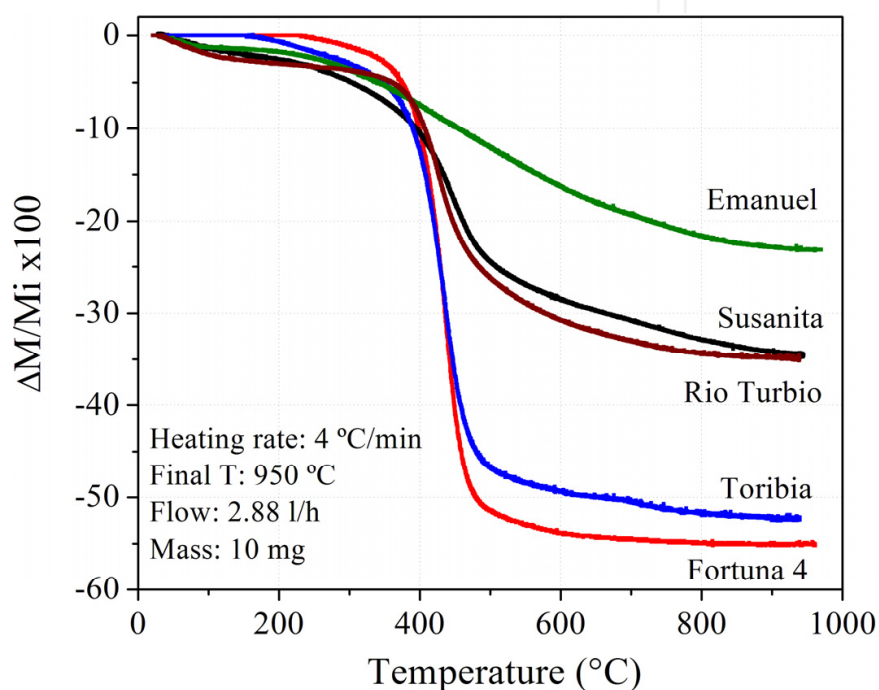

Figure 5. Thermo-gravimetric curves of non-isothermal pyrolysis tests with argon.

The comparative behaviour of Río Turbio coal and asphaltites under CO_2 gasification conditions was studied by performing non-isothermal and isothermal TGA measurements. The non-isothermal TGA curves are presented in Figure 6 and the experimental conditions were: temperature range between room temperature and 950 ˚C; heating rate of 4 ˚C/minute; partial pressure of CO_2: 80kPa; and sample mass: 10 mg.

It can be observed that the mass losses measured are due to the release of adsorbed water at low temperature (about 100 ºC) while, at higher temperatures (above 600 ºC), the mass losses corresponded to the gasification reaction of chars with CO_2, producing mainly CO(g). The initial reaction temperatures were: 630, 650, 680, 700, and 730 ˚C for Susanita, Emanuel, Río Turbio, Toribia, and Fortuna 4, respectively. These temperatures are indicative of the reactivity of chars, meaning that Susanita asphaltite has the highest reactivity and Fortuna 4 asphaltite has the lowest reactivity. Moreover, Toribia and Fortuna 4 asphaltites did not achieve the complete gasification when the temperature reached 950 ºC, showing a reduced reaction rate for the two samples. The other three chars presented a similar mass loss.
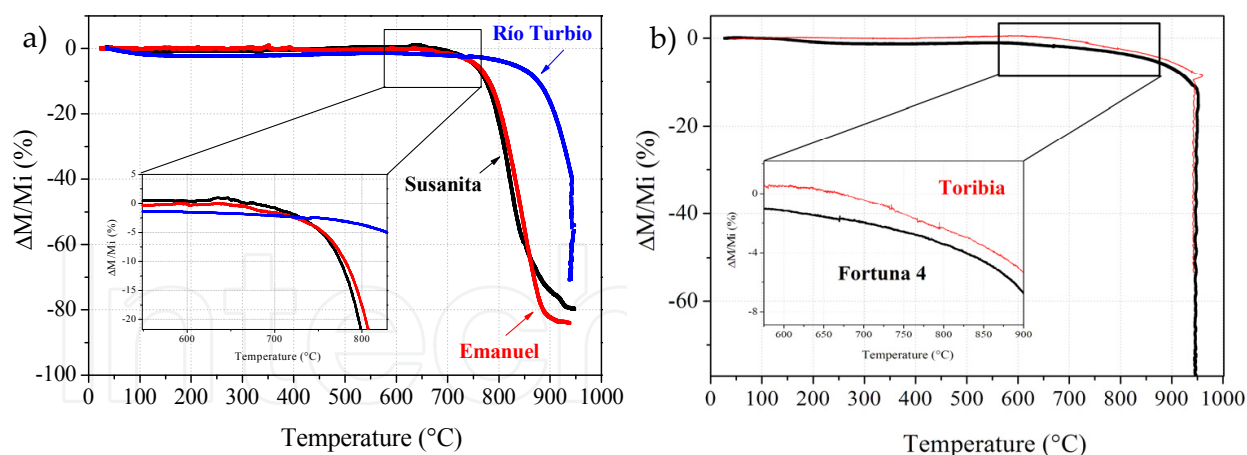
Figure 6. Thermo-gravimetric curves of non-isothermal gasification experiments with CO2.

In order to study the kinetics of the gasification process, isothermal TGA curves must be obtained. Figure 7 shows the isothermal TGA curves corresponding to the CO2 gasification of chars obtained in the non-isothermal pyrolysis tests. The experimental conditions were: temperature: 875 ºC; partial pressure of CO2: 80 kPa; total gaseous flow rate [Ar - CO2] :10 l/min, and initial sample mass: 25 mg.
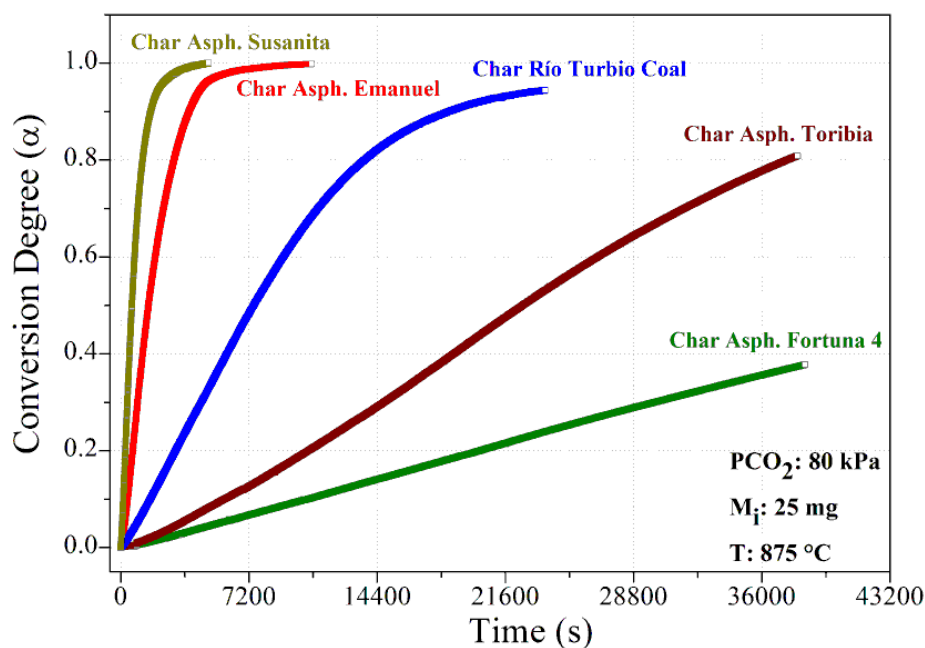

Figure 7. Thermo-gravimetric curves of isothermal gasification experiments with CO2.

The wide range of reaction rates observed for these solid fuels (almost two orders of magnitude between Fortuna 4 and Susanita asphaltites) is indicating that they have different reactivities in presence of CO2, and the difference may be attributed to the content of fixed carbon and mineral matter. As can be seen in Figure 7, Susanita and Emanuel asphaltites have a similar fixed carbon content, the same happens with Toribia and Fortuna with a lower fixed carbon content, while Río Turbio coal has an intermediate value. Related with

the fixed carbon content, the most important effect that can be taken into account is the presence of more amounts of C-C bonds that may signify a greater net energy bond due to the absence or low content of impurities that can produce defects in the solid fuel matrix, increasing the reactivity with the CO_2.

In order to compare the relative influence between the fixed carbon content and the surface area of chars on the gasification rate, the BET areas were determined on chars obtained from Emanuel asphaltite and Río Turbio coal. Even the exposed surface area of Río Turbio char is almost 30 times higher than the Emanuel asphaltite one, the complete gasification reaction occurred after about 6 hours and 1 hour, respectively. This result indicates that the surface area has less influence on the reaction rate compared to the fixed carbon content of the feed material.

Other important characteristics which have a remarkable effect on the gasification rate are the elemental mineral matter and the mineral phases contained in the chars, since it is well-known that mineral matter naturally present in the carbonaceous matrix may act as a catalyst for the gasification reactions. As shown in Table 1, Fortuna 4 and Toribia asphaltites have very small amounts of mineral matter (ash content below 2 wt%), and they presented the lowest reaction rates. Emanuel asphaltite, even having a relatively low mineral matter content and a low BET area (7 wt% of ash and 3.5 m²/g), has the highest diversity of metals such as V, Mo, Sr, Ni, and Cu among others, and then the catalytic effect of these metals could lead to the high reactivity observed in experiments. The same explanation can be applied to Susanita asphaltite which has a high ash content and also a fairly diversity of metals, showing the highest reactivity in presence of of CO_2. Finally, the reactivity of Río Turbio coal is intermediate between asphaltites of high and low mineral contents. A further catalytic effect that could be observed from the XRD measurements is that those chars containing calcium sulfate show higher reaction rates than those which have calcium forming other compounds.

6.3. Effect of gasification temperature and partial pressure of gasifying agent

From TGA and GC isothermal measurements obtained at several temperatures, partial pressures of reactants, and using CO_2 and steam as gasifying agents, the kinetic parameters of the rate equations of the gasification reactions could be determined.

In the method proposed by Flynn (Basan S. 1986), the activation energy can be determined from equation (5), although $G(C_g)$ and $f(X)$ are unknown functions. Replacing $K(T)$ by an Arrhenius equation and rearranging equation (5):

$$\int_0^\infty \frac{dX}{f(X)} = \int_0^t G(C_g) A \exp(-E/RT) dt \tag{14}$$

after taking the integral, we have:

$$F(X) = G(C_g) A \exp(-E/RT) t \tag{15}$$

and by taking the logarithm of both sides of equation (15):

$$\ln t = \ln\left[\frac{F(X)}{G(C_g)A}\right] + \frac{E}{RT} \qquad (16)$$

The first term in the right hand side of equation (16) is a function of degree of reaction and partial pressure of carbon dioxide. Therefore, if partial pressure of carbon dioxide is keep constant, and the time to attain a certain reaction degree is determined as a function of temperature, equation (16) allows to obtain the activation energy from the slope of the plot $\ln t$ vs. T^{-1}. Analogous procedure can be applied to obtain the reaction order with respect to gaseous reactant replacing $G(C_g)$ by a power law expression. The reaction order can be obtained from the slope of the plot of $\ln t$ vs. C_g

By this method (also known as model-free method or iso-convertional method), the activation energies of gasification reactions were obtained and results are shown in Table 3, while the $\ln t$ vs. T^{-1} plots are shown in Figure 8.

The activation energies calculated are consistent with the fact that the Río Turbio coal showed a lower reaction rate compared to Emanuel asphaltite. Furthermore, the similar values of the activation energies for gasification reactions with CO_2 and steam show that the determining step in the mechanism of these reactions is independent of the gasifying agent used, and it can be associated more with the restructuring of carbon surface than with the gasifying agent accommodation.

Solid fuel	Activation energy	
	Gasification with $CO_2(g)$	Gasification with steam
Río Turbio coal	190 ± 10 kJ/mol	na
Emanuel asphaltite	185 ± 10 kJ /mol	186 ± 10 kJ/mol

na: not available

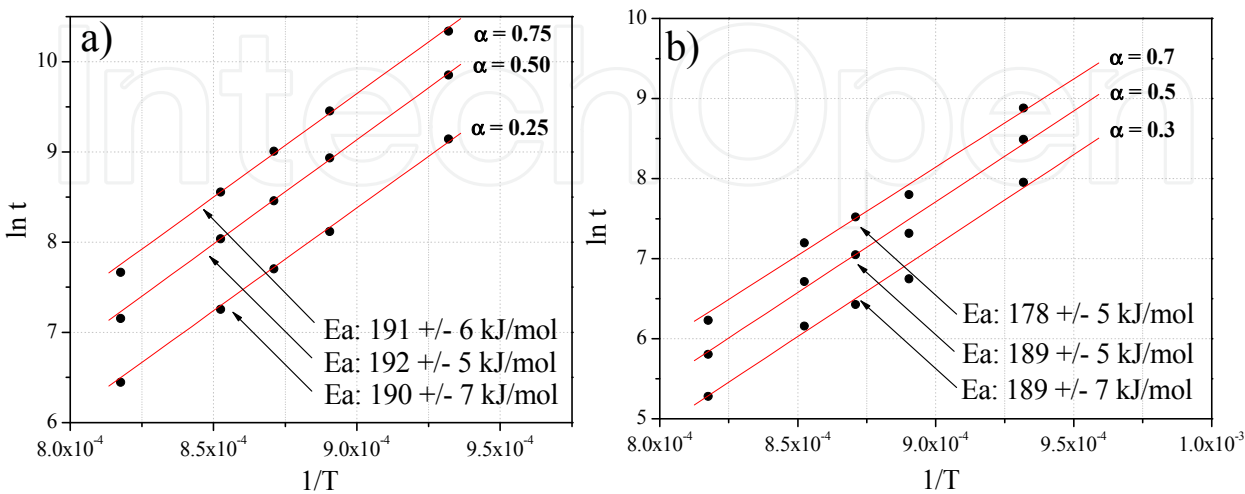**Table 3.** Activation energies of gasification reactions with CO_2 and steam.

Figure 8. ln t vs. 1/T plot for the calculation of Ea with the Flynn method. (a) Río Turbio coal; (b) Emanuel asphaltite.

The reaction order (n) with respect to the gasifying agent was only determined for CO_2 gasification reactions and results are presented in Table 4 and Figure 9. The reaction order is 1 for the Río Turbio coal and 0.5 for the Emanuel Asphaltite. The first value may indicate that the reaction with CO_2 is produced by occupying only one active site on the surface while, on the opposite, the second value is indicating that a dissociate step on the surface of the particle may be occurring, with the CO_2 molecule being adsorbed and occupying two active sites. The last mechanism requires less activation energy for the breakdown of the C-O chemical bond than the first one, so the gasification reaction is expected to be faster, as it was already shown in the isothermal TGA curves

Solid fuel	Reaction order with respect to reactant	
	Gasification with $CO_2(g)$	Gasification with steam
Río Turbio coal	1	na
Emanuel asphaltite	0.5	1

na: not available

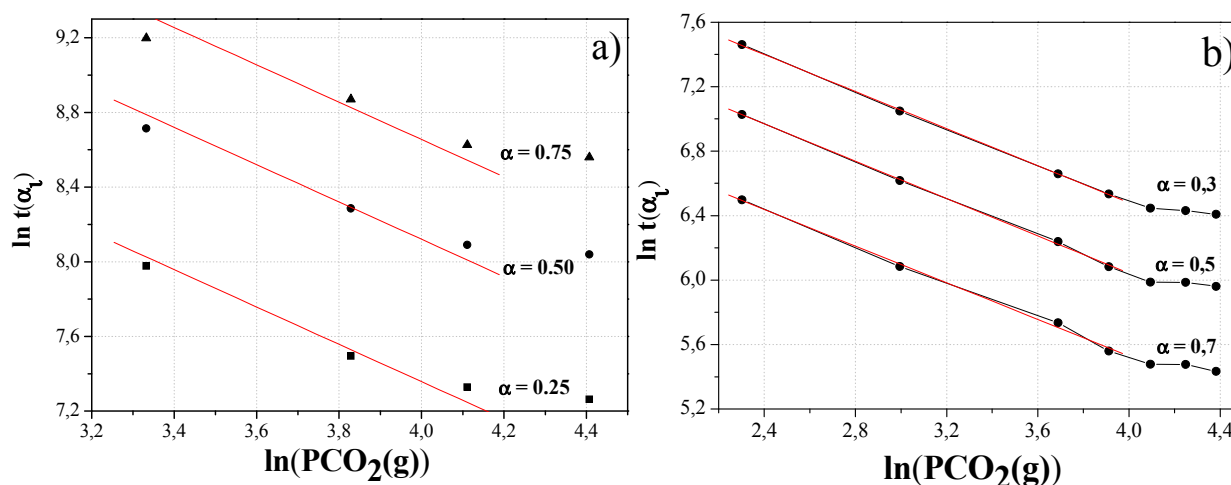**Table 4.** Reaction order of gasification reactions with CO_2 and steam.

Figure 9. ln t(αi) vs. ln(PCO_2) plot for the calculation of the reaction order with respect to reactant. (a) Río Turbio coal; (b) Emanuel asphaltite.

6.4. Effect of gasifying agent

A comparative analysis of reactivity of Argentine solid fuels in presence of CO_2 and steam was also performed and main results are summarized in Figure 10. Figure 10(a) shows the conversion degree vs. time in TGA curves obtained from Emanuel asphaltite chars gasified at 875 ºC with CO_2 (at a partial pressure of 80 kPa) and steam (at a partial pressure of 20 kPa), respectively. It can be appreciated that the steam reactivity of Emanuel asphaltite char is a little bit higher than CO_2 reactivity even the steam partial pressure used in experiments was lower than the CO_2 partial pressure.

On the other hand, Figure 10(b) shows the conversion degree vs. time in curves obtained from Río Turbio coal chars gasified at 875 ºC in the tubular reactors shown in Figures 3 and

4. In this case, the difference in gasification reactivity between steam and CO_2 is more significant and matches better with the results found in literature (Roberts, D.G. 2000 and Messenbock, R.C. 1999).
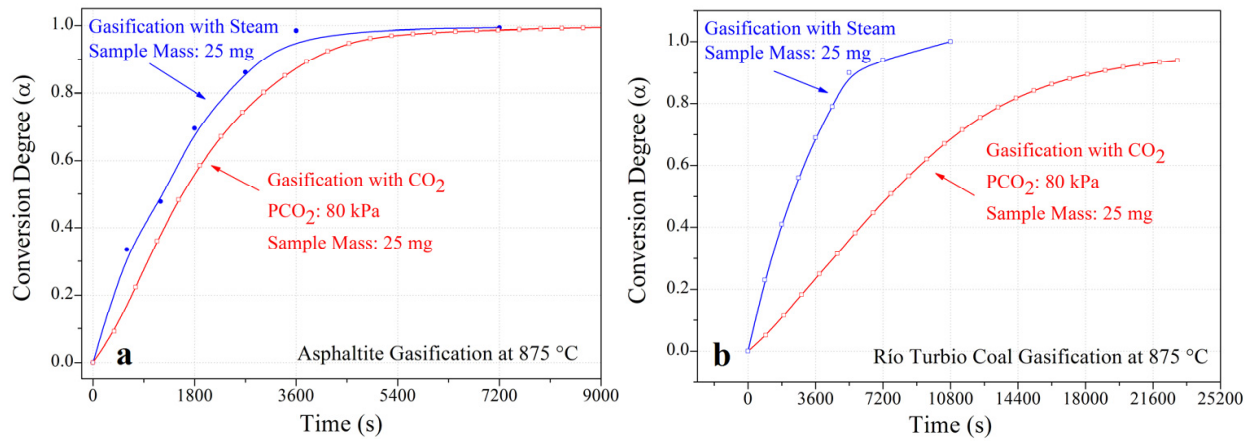

Figure 10. (a) TGA curves of Emanuel asphaltite char gasified with steam and CO_2; (b) gasification curves of Río Turbio coal char gasified with steam and CO_2 in tubular reactors.

6.5. Effect of char formation conditions

Chars from Río Turbio coal were prepared in three different conditions: (1) in the DTF at 850 ºC; (2) in the DTF at 950 ºC; and (3) in a Fixed Bed Reactor (FBR) at 950 ºC. Following, 10 mg of each char sample was gasified at 900 ºC in the TGA system with 30% CO_2 partial pressure at the same flow rate, in order to compare their gasification reactivities.
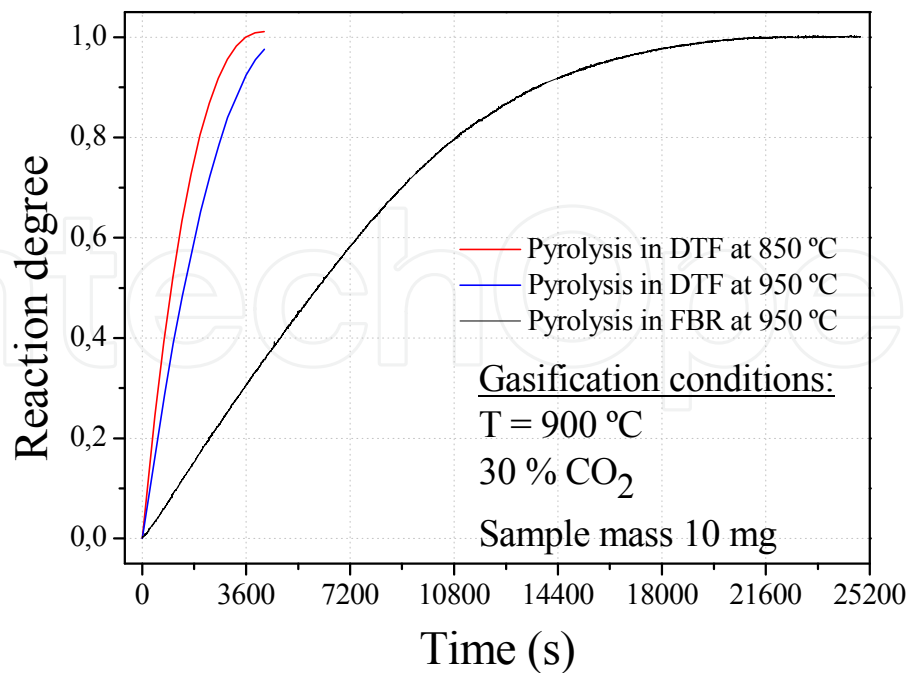

Figure 11. TGA isothermal CO_2 gasification curves of Río Turbio chars prepared in different pyrolysis conditions.

Figure 11 shows the TGA isothermal curves corresponding to the three different chars. It can be observed that both chars pyrolysed at high heating rates in the DTF followed a similar behavior and the gasification reactivity is comparable to reactivities of low-rank coals used in large-scale gasifiers. On the opposite, the TGA curve corresponding to the char prepared at low heating rate in the FBR shows that the gasification reaction progressed much slowly and it was completed after a long time, indicating a very low reactivity in presence of the gasifying agent.

These experimental results are demonstrating that the reactivity of chars to gasifying agents is very dependent on their formation conditions and, then, to get meaningful data about kinetics of gasification reactions, it is very important to produce chars in laboratory at high heating rates and intense gas convection around individual char particles, replicating the real operating conditions of commercial gasification reactors.

Finally, the reaction rate as a function of the conversion degree for those gasification experiments is presented in Figure 12, which also shows the predicted values by the grain model superimposed to the experimental measurements. It can be appreciated that the grain model is expected to well-simulate the gasification behavior of the Río Turbio coal in the temperature range used in experiments. From these fittings, the kinetic parameters of the theoretical models were calculated and they are given in Table 5.
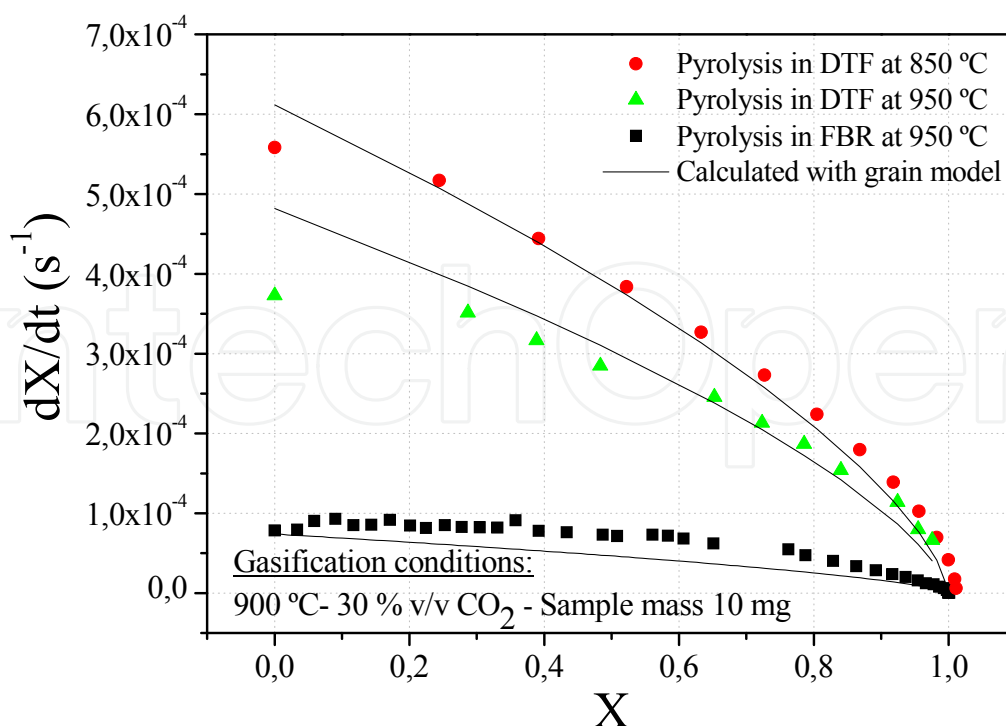

Figure 12. Theoretical and experimental CO_2 gasification rates of Río Turbio chars prepared in different conditions.

Char preparation	Model free method	RPM				GM	
		$\dfrac{dX}{dt} = k_0 e^{-\frac{E_a}{RT}}(1-X)\sqrt{\left[1-\psi\ln(1-X)\right]}$				$\dfrac{dX}{dt} = k_0 e^{-\frac{E_a}{RT}}(1-X)^{\frac{2}{3}}$	
	Ea kJ/mol	Ea kJ/mol	k_0 s⁻¹	Ψ		Ea kJ/mol	k_0 s⁻¹
Pyrolysis in DTF at 850 ºC	171 ± 10	165 ± 11	$1.15\ 10^4$	2		166 ± 11	$1.51\ 10^4$
Pyrolysis in DTF at 950 ºC	159 ± 22	158 ± 2	$4.07\ 10^3$	2		158 ± 2	$5.24\ 10^3$
Pyrolysis in FBR at 950 ºC	190 ± 10	na	na	na		195 ± 12	$3.6\ 10^4$

Table 5. Kinetic parameters of theoretical models used for simulating the gasification reactions.

It can be observed that the activation energy values of the gasification of chars prepared in the DTF are lower than the value corresponding to the char prepared in the FBR. Meanwhile, the values of the reaction rate constant are similar in all cases, independently of the char preparation method. These values are in agreement with the fact that the gasification reactions of chars prepared in DTFs are faster than the gasification reactions of chars which are pyrolysed in FBRs. Another important aspect is that the activation energy has the most significant effect on the char gasification rate in the present experimental conditions.

7. Conclusions and future works

A comprehensive theoretical and experimental research program is being implemented in Argentina at laboratory scale in the framework of a national strategy for the integral utilization of its domestic coal reserves, addressed to bring together the requirements of a sustainable economic growth with the environmental protection. The research program was designed to simulate in laboratory, as close as possible, the operational conditions of large-scale gasification plants and, then, to provide the necessary information about fundamental mechanisms and kinetics of the gasification reactions for a further scaling up of experimental facilities. For this purpose, specially-designed experimental equipment and test procedures were implemented for gasification experiments using carbon dioxide and steam as gasifying agents.

Experimental program on gasification with carbon dioxide is almost finished and experimental results show that all the Argentine solid fuels studied are amenable to be gasified since their gasification reactivities at high heating rates are comparable with those of low-rank coals used in large-scale gasifiers. Experimental program on steam gasification is just beginning but preliminary experimental results show that the reaction rate is higher than the reaction rate corresponding to the gasification with carbon dioxide.

As it was detected that some mineral phases present in the ashes may have a catalytic effect in gasification reactions, further studies to elucidate this influence are planned for the

future, along with the construction of experimental setups for carbon dioxide and steam gasification experiments at higher pressures.

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