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Carbon based catalytic briquettes for the reduction of NO: Catalyst scale-up

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Abstract

Exhaust gasses from small and medium stationary sources contain NO_x that will be regulated by new European legislation in the coming years. Among all the processes the SCR-NH_3 seems to be the more promising one. However, the application of commercial catalysts to these new facilities presents some drawbacks such as the high and narrow operation temperature, its low withdraw to SO_2 or its high cost production.

In order to improve this technology, in previous works, carbon-supported catalytic briquettes have shown a good kinetic performance under the above commented conditions. In this study, other aspects such as thermal stability, long-term performance, spatial velocity influence and mechanical resistance were evaluated. Finally, a simple economic assessment was carried out providing a three times lower cost production than commercial catalysts. From all the data collected, there are some evidences that these catalyst briquettes will have a good performance in small and medium facilities, being an interesting alternative to commercial ones.

Keywords: Briquette; Carbon based catalysts; SCR-NH_3

1. Introduction

Exhaust gases from stationary and mobile combustion sources contain NO_x that cause a variety of environmentally harmful effects. Taking into account these problems, governments from developed countries propose an each stricter legislation in the coming years that will also affect to the medium and small stationary sources like IGCC plants, static diesel engines or adiptic acid production plants.

Among all the technologies the selective catalytic reduction (SCR) of NO_x by NH_3 has gained eminent importance because of its high efficiency. However, it is widely known that, nowadays this technique, with the available commercial catalysts, implies an important economic effort for all medium–small stationary sources. Moreover, the current TiO_2 supported catalysts present very serious drawbacks to be successfully installed in this kind of facilities. In the high temperature window (300–500 °C) where they operate, SO_2 and particle poisoning are great disadvantages [1]. In addition, the effluent gas should be re-heated after the particle removal equipment and the desulfuration device, because at this point the temperature is about 250 °C, being this fact an extra operation cost. Understandably, therefore, there is an increasing interest in developing low temperature catalysts (<250 °C) capable of working without the need for re-heating the gas. Eventually, it would be desirable that these novel catalysts have a good mechanical performance, thermal stability, long performance as well as a low production cost.

Carbon has been studied as catalyst support for the low temperature SCR of NO_x by a number of authors [2–4] due to its high surface area, chemical stability and good performance. Moulding this support into a structured shape with low pressure drop presents some advantages over powder conventional catalysts. According to these objectives, a procedure for preparing catalysts supported on low-rank coal briquettes with coke petroleum ashes (PCA) as an active phase has been developed [5]. PCA contains a high amount of vanadium, iron and nickel among other transition metals showing a good performance in the low temperature SCR [6–8]. In previous works, really interesting results have been found for low-rank coal briquettes doped with PCA [5]. In these studies, considerable activity and selectivity were reported at temperatures between 150 and 250 °C, in presence of ammonia and oxygen excess and in addition, they presented kinetic

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parameters similar to other catalysis reported in literature and proposed for the same application [6]. In the present paper, catalytic briquettes prepared as described in Ref. [5] are tested in a bed fixed reactor, economically evaluated and taken into account their thermal stability, long performance, spatial velocity influence and mechanical properties. Therefore, the main aim of this work is to analyze the suitability of this new product for medium–small stationary sources considering different topics apart from the kinetic ones to know if the product could have been easily introduced into the market.

2. Experimental

2.1. Preparation of the catalytic briquettes

The main materials used to produce catalysts have been described in more detail elsewhere [9]. In a few words, a low-rank coal, from SAMCA mines in Teruel, Spain, and a commercial pitch of SP-110 were ground and sieved, subjected to pressure briquetting process, pyrolyzed and subsequent activated as it is described in elsewhere [10]. Two major types of catalytic briquettes were produced: (1) briquettes with an oxidized carbon support and (2) briquettes with a non-oxidized carbon support. The oxidation procedure was carried out before the impregnating one with 1N acid nitric solution. Oxidized samples were named adding-+HNO_3 to the activation name. A coke from the Delayed Coke unit in the REPSOL refinery in Puertollano, Spain, was used for the production of the PCA, as it was explained in elsewhere [11]. The PCA contain 23% (w/w) of V, 3.5% (w/w) of Fe and 3% (w/w) of Ni among other transition metals [12]. The briquettes were impregnated by equilibrium adsorption of 3% (w/w) vanadium.

2.2. Thermal stability

Support and some catalytic briquettes were characterized by thermogravimetric analysis in a CAHN TG 2151 equipment. A piece (around 200 mg weight) was heated under a heating rate of 10 °C/min in an Ar flow of 2000 cm^3/min from room to desired test temperature. When test temperature was reached, gas reaction mixed consisting of 1000 ppmv NO, 1500 ppmv NH_3 and 3.5% (v/v) O_2 in Ar was introduced and maintained for approximately 2 h. Weight loss was calculated as a percentage from the stable weight once reaction temperature was reached.

2.3. Mechanical characterization

Mechanical strength was tested by means of impact resistance index (IRI) and water resistance index (WRI), as described in Ref. [13]. The IRI values were as a function of the number of drops and the number of pieces into which each briquette breaks when it is repeatedly dropped from a stationary starting point at 2 m height onto a concrete floor until it fractured. The WRI values were obtained immersing a weighted briquette in cold tap-water and checking for any tendency to disintegrate.

2.4. Catalytic measurements

All the samples were tested for NO reduction with a mass spectrometer (Quadrupole Balzers 422) connected online as detection system. The mass spectrometer was calibrated using known standard cylinders. Long-term performance, spacial velocity influence as well as catalytic activity tests were carried out in a quartz reactor of 7 mm of diameter with a catalysis weight of 0.4 g. Standard conditions fed to the reactor were 1000 ppmv of NO, 1500 ppmv of NH_3 and 3.5% (v/v) of O_2 in Ar. The NO reduction efficiency was calculated as follows:

$$\%\,\mathrm{NO\,reduction} = \frac{C^{i}_{NO} - C_{NO}}{C^{i}_{NO}} \times 100 \qquad (1)$$

where C^{i}_{NO} is the measured initial concentrations of NO and C_{NO} corresponds to its concentration once steady state is reached.

2.5. Economic assessment

The economic analysis was carried out by reckoning the costs of investment, energy and other operation costs necessary to set in a factory which produces 1 t per day of catalytic briquettes. The briquette production factory is assumed to be consisted of carbon millers, coke millers, tar millers, blenders, briquetting machines, curing ovens as well as drying ovens, fixed bed for activation and pyrolysis of briquettes, tanks for the impregnation of the support and finally a packing machine as shown in Fig. 1. In the same way, it will be necessary to provide the factory with auxiliary equipment such as compressors, heat exchangers, a boiler, IGCC and piping. Information was obtained from industrial suppliers as well as from other chemical industries which are operating at present. Apart for the investment and operation costs a rough feasibility analysis was carried out taking into account the most common parameters for this kind of production plants.

3. Results and discussion

Since the aim of this work was to evaluate catalytic briquettes for their operation in small and medium stationary NO_x sources some aspects apart from kinetic ones, evaluated in previous works [5,6,14], are discussed below.

3.1. Thermal stability

One of the main drawbacks of carbon supports, previously reported in the literature [15,16], is the lower withstand to temperature in comparison to metal oxide based catalysts. In order to evaluate thermal stability of catalytic briquettes and support some thermogravimetric tests were carried out. First of all, the thermal stability of carbon support was considered as reported in Ref. [14]. For this purpose, a briquette activated at 700 °C (2 h with a 20% steam in N_2) was heated up at three different temperatures as shown in Fig. 2. Even at the highest temperature (400 °C) carbon support does not shown any

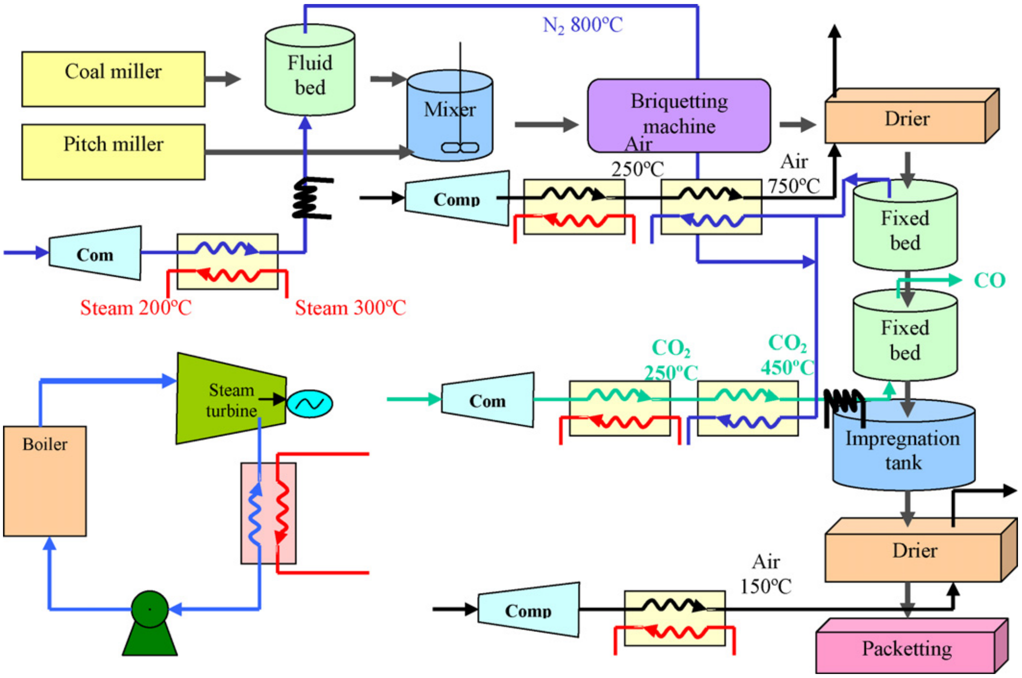

Fig. 1. General lay-out of a 1 t/day production plant of catalytic briquettes.

weight loss which could be considered as a proof against carbon combustion. Moreover, after 2 h reaction, there seems to be a slightly increase of weight, which could be due to the formation of some oxygen superficial groups.

Equally, thermal stability of two catalysts doped with PCA or V_2O_5 was tested at 400 °C. Catalyst doped with PCA shows a slightly weight loss whereas catalyst doped with V_2O_5 remains unaltered. This fact could be due to the different nature and dispersion of the active phase, which is able, to some extend, to catalyze the carbon oxidation reaction. Fig. 3b shows the influence of oxidation process on thermal stability. Oxidation process seems to speed up the support combustion reaction which could be due to a change in the active phase anchoring. Anyway, when thermogravimetric tests are carried out at lower temperatures (300 °C), there is no significant weight loss. Finally, a long-term thermogravimetric test was carried out subjecting a briquette to reaction for around 20 h at 400 °C (Fig. 3b). A weight loss of around 7% was detected which, taking into account the high temperature, could ensure a good performance of this catalyst in industrial facilities.

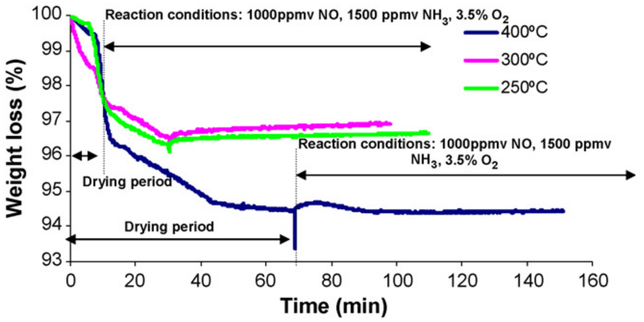

Fig. 2. Thermal stability of Br/A/700 °C/2 h/H_2O support.

3.2. Long-term activity tests

Like thermal stability, long-term performance maintaining NO conversion is required for its application in industrial facilities. In previous works [5,6], catalytic briquettes tested under different temperatures for 2 h shown NO reduction between 38 and 80%. In this study, the catalytic stability of

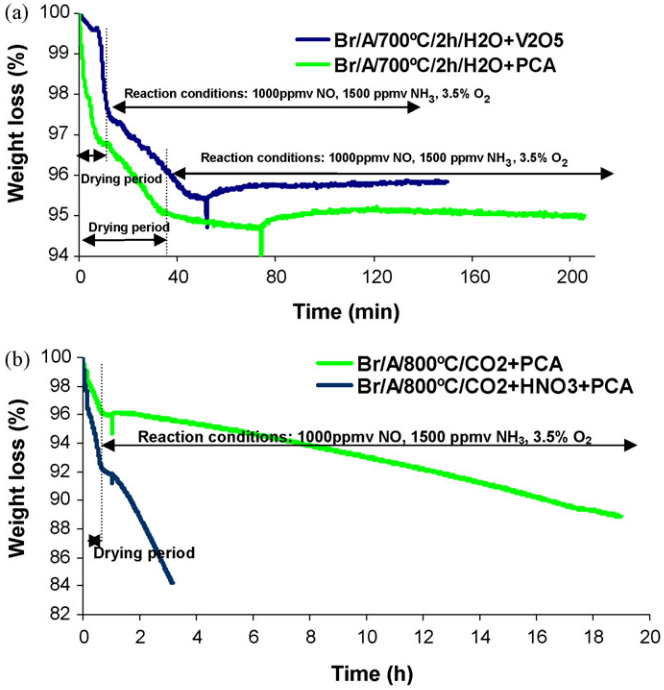

Fig. 3. Thermal stability of (a) Br/A/700 °C/2 h/H_2O + PCA and Br/A/700 °C/2 h/H_2O + V_2O_5 catalysts and (b) of Br/A/800 °C/1 h/CO_2 + HNO_3 + PCA and Br/A/800 °C/1 h/CO_2 + PCA catalysts.

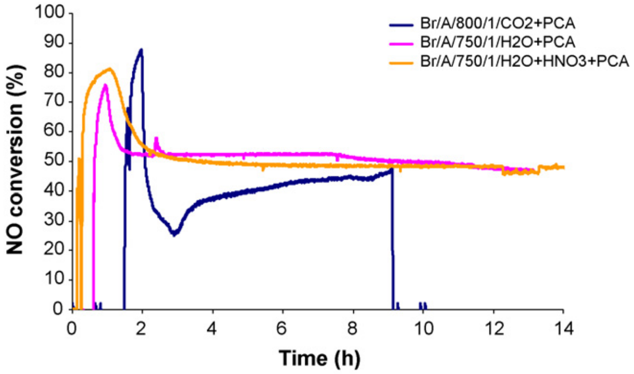

Fig. 4. Long-term performance of Br/A/800 °C/1 h/CO_2 + PCA and Br/A/800 °C/1 h/CO_2 + PCA catalysts (12 h operation).

briquettes was tested after 12 h on stream, as shown in Fig. 4. The starting peak can be due to instability of mass flow meters when getting to the set point. These values were not taken into account when reporting NO conversions values. As catalytic activity remind constant for this short period a higher one was tested for the briquette Br/A/800 °C/1 h/CO_2 doped with PCA. Fig. 5 shows that its conversion did not change too much after 24 h on stream which provides a further evidence for its installation in industrial facilities. NO conversion from oxidized samples is without any doubt much more instable than that of non-oxidized samples. This fact can be due to the higher among oxygen surface groups created by means of acidic treatments that modify the adsorption of NH_3 along the runs depending on their release and the temperature at which the reaction is carried out. Maybe it could also due to possible instabilities of the flow mass meters and temperature controllers when experiments were run without supervision.

3.3. Spatial velocity influence and fixed bed reactor tests

The influence of spatial velocity in the catalytic conversion is a key factor for a good performance of these catalysts in facilities with a wide range of operational conditions. Spatial velocity influence was tested for two catalysts, Br/A/750 °C/2 h/H_2O and Br/A/800 °C/1 h/CO_2, both doped with PCA. Fig. 6 shows that the higher the GSHV the lower the conversion. For a GSHV of 1000 h^{-1} a conversion of 50% is reached whereas a GSHV of 9500 h^{-1} allows a conversion of around 40%.

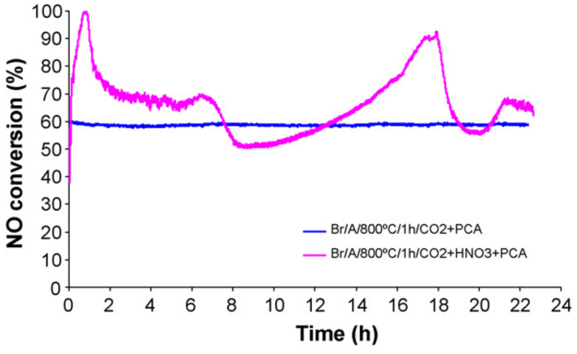

Fig. 5. Long-term performance of Br/A/800 °C/1 h/CO_2 + PCA and Br/A/800 °C/1 h/CO_2 + PCA catalysts (24 h operation).

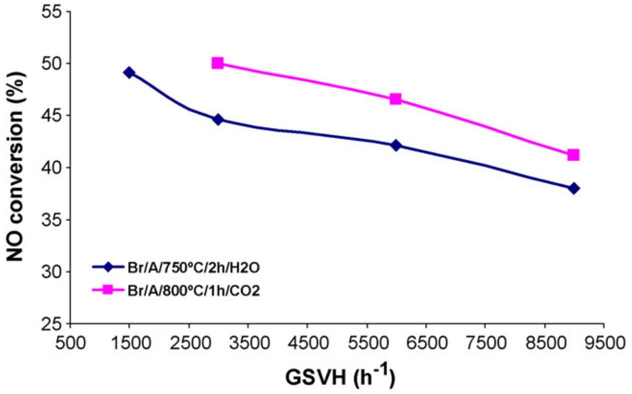

Fig. 6. Influence of spatial velocity on Br/A/700 °C/2 h/H_2O reduction activity.

3.4. Mechanical properties

As previously reported [14], preparation process steps influence their mechanical properties, especially those of duration, pyrolysis, activation and oxidation, by changing textural and surface chemistry properties. In Fig. 7, IRI and WRI values are plotted for a series of activated briquettes under different conditions. As the target value for IRI is taken to be 50 [13], all briquettes pass this test but it can be seen that activation process influences greatly on their mechanical properties. Generally speaking, the more severe the activation process is, the lower the IRI, which is more noticeable in the case of steam activation. Regarding the textural properties of samples presented in previous works [5,6], steam activation causes a lineal increase of micropore and an exponential increase of mesoporous volume from samples activated at 700 °C on. Relating both trends with the IRI lineal decrease, there is no doubt that IRI values are more dependent on microporosity than on mesoporosity. This trend agrees with another author [17] who found out a decrease of IRI values when a higher microporosity was developed. According to this information, the activation at lower temperatures influences positively the IRI.

On the other hand, WRI values are greatly influenced by the presence of oxygen surface groups. Taking into account WRI values shown in Fig. 7b, a temperature increase in the activation process causes a decrease on WRI indexes. This fact could be due to the higher amount of acidic functionalities and an acidification of surface. These results agree with another author [18] who considered disintegration as a result from competition between the tendency of coal particles to swell, favored by surface hydrophilic groups, and the binding force between particles to maintain the briquette integrity, favored by carboxyl groups on surface. Fig. 7a shows WRI values of oxidized briquettes in comparison to non-oxidized ones. WRI values of oxidized briquettes are lower which can be related to the higher amount of oxygen surface groups created. Acid treatment provides to carbon a higher hydrophilic surface which enhances water adsorption and speeding up the disintegration of the briquette.

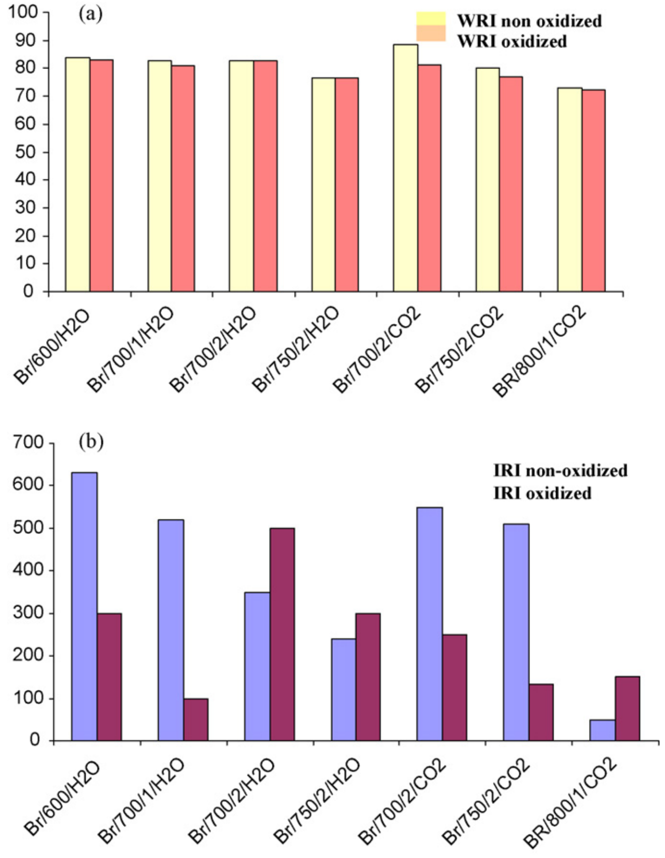

Fig. 7. Results of mechanical characterization. (a) Values of impact resistance index (IRI) of oxidized and non-oxidized samples and (b) values of water resistance index (WRI) of oxidized and non-oxidized samples.

Finally, oxidation process influences IRI of briquettes as well. Results of IRI runs are shown in Fig. 7b which change in a particular way. This fact could be related to the decrease in surface area and micropore volume as reported in Refs. [5,6,14]. Whether activated samples have a well-developed microporosity, a decrease of structural features provides an increase of IRI, while if activated samples have a poorly developed microporosity a decrease of this property causes a decrease in IRI values. Both trends suggest the existence of an optimal point in microporosity development where the briquette supports will show the highest IRI. This optimal point should be centered neither at lower microporosity where propagation of cracks is favored nor at higher microporosity where particle connexions are so weak that do not allow high IRI.

3.5. Economic assessment

As commented in Section 2, the economic assessment was performed taking into account the facilities shown in Fig. 1. The costs for the millers, fixed bed, ovens, heat-exchangers as well as compressors were derived from Ref. [19], the cost of the cogeneration system was based on judgment considering earlier data [20] and the cost of briquette machine was obtained directly from Komarek Inc. Costs associated with auxiliary equipment were based mainly on Ref. [21] which displays detailed breakdowns of a variety of chemical systems. It includes site development, infrastructure, pipping, instrumentation and control, security provisions, contingency, etc. The O&M cost is taken to be 2% of the capital cost for the first 10 years and 5% from the 11 year on. Costs of lands surface and buildings were leaving aside because they are highly dependent on geographical area to be set in. Government subsidies have been excluded from consideration. Also not accounted for is any cost incurred from storage of raw materials and products and it is only taken into account a transportation cost of raw materials for 200 km far by road. Table 1 shows the facilities and raw material costs. In order to obtain PCA from the petroleum coke a boiler was supposed to be installed. The heat produced from PC is recovered in an IGCC with a supposed efficiency of 60%.

The catalytic briquette production size is selected to be one that delivers 1 t/day for making easy to reckon the costs. From these data, an estimated market price was calculated. It was assumed the following economic rates: 20% of the investment cost is own, the interest rate will be constant at 5.5% for 20 years, the amortization rate will be lineal for 20 years and finally a constant inflation rate of 3% is considered. In order to take into account profitable conditions for the catalytic briquette production plant a TIR of at least 8% was supposed. The resulting estimated market price is 2.8 €/kg of catalytic

Table 1
Facilities and operation costs for a production plant of 1 t/briquettes per day

Equipments	Initial investment for a production factory of 1 t/day	Energy consumption	€/t briquette	Raw materials	€/t briquette
Millers	180.000 €	Coal miller	1.758	Coal	0.524
Fluid bed	34.977 €	Coal miller 2	2.194	Pitch	1.438
Mixers	60.000 €	Pitch miller	0.160	Coke	20.7065
Briquetting machine	195.000 €	Coke miller	34.222	Nitric acid	
Furnace	769.063 €	Coal preparation	36.440	CO_2	0.117
Fixed bed	69.954 €	Coal homogenization	0.309	Water	1.333
Impregnation tank	79.916 €	Pitch homogenization	0.053	N_2	0.117
Driers	743.244 €	Fixed bed	517.78	Man power	702.40
Compressors	$2_1$413.411 €	Driers	711.53	Coal transportation	2.342
Cogeneration equipment	$1_1$713.000 €	Briquetting machine	32.38	Pitch transportation	0.462
Heat exchangers	13.467 €	Compressors	1.93	Coke transportation	170.434
Auxiliary equipments	50%	Packetting	0.51		
Fields	136.000 €	Auxiliary equipment	20.32		
Total	$9_1$702.052 €		1359.59 €		899.876 €

briquettes. The weakness of this economic assessment is primarily related to the uncertainties in efficiencies and investment costs due to their new application of this catalytic briquette production factory and to its economy scale.

The catalytic briquette cost was compared to that of commercial catalysts produced from TiO_2 supports in a specific application. IGCC conditions [22] have been chosen (25 mg/Nm^3 of SO_2, 250 mg/Nm^3 of NO_x and 537 kg/s of effluent gases). As far as the catalytic briquettes are concerned, it is needed a total weight of 616,948 kg to reach a NO reduction of 85% at 250 °C which involves a costs of 1,850,000 €. For the same application, the cost of a commercial catalyst [23], getting a NO reduction of 85% at 350 °C, rises to 6,160,000 € which is approximately three times higher. However, it is worth taking into account that the temperature required in the catalytic briquette system is much lower than the temperature of the commercial catalyst and likely no re-heating system is required. As it could be seen, the proposed catalytic briquettes could be competitive with the commercial catalysts, provided that their lifetime operation is as long as the one of commercial catalysts.

4. Conclusions

The results of this work may allow devising processes for a proper utilization of carbon-based briquettes, which is a very important issue for air pollution abatement from small and medium facilities. The use of carbon-based catalytic briquettes, prepared from low-rank coal and petroleum coke ashes, is presented as an interesting alternative to high cost commercial catalysts based on metal oxides. Catalytic briquettes show a high thermal stability, with a good resistance to carbon combustion even at higher temperatures than those for which they were proposed to. Thermal stability is negatively affected by oxidation and impregnation steps although both steps are essential to get a higher NO reduction. Long-term performance tests guarantee a stable catalytic conversion under the tested conditions for at least 24 h without sign of deactivation. Spatial velocity influences catalytic activity decreasing the NO reduction. This fact has also been widely investigated by other authors proposing this kind of catalyst for slow flow installations.

From the point of view of the mechanical strength, it can be concluded that mechanical properties depend strongly on the activation and oxidation process, due to the textural and surface chemistry properties developed during these processes. IRI values dependent on microporosity volume though WRI is more dependent on surface chemistry. Optimal IRI values seem to be between low microporosity values where cracks are easily propagated and high microporosity where the connections between particles are really weak. On the other hand, carboxyl groups favors higher WRI values whereas the creation of a high amount of oxygen surface groups that provides a higher hydrophilic surface decreases WRI values.

Finally, a simple economic assessment was carried out to provide a rough cost production. Taking into account raw materials, energy, facilities mortgages as well as other operation and transportation costs a final cost of 2.8 €/kg was provided. This value was compared to that of a commercial catalyst for an IGCC application resulting three times less expensive. Despite this fact, evidences are not enough to ensure that it could be successfully introduced into the catalyst market until more aspects such as lifetime operation, flow dynamic or mass transfer in a fixed bed reactor were evaluated.

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