

Catalytic Pyrolysis of Biomass

Eucalyptus Sawdust Gasification

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Catalytic gasification of Eucalyptus sawdust was studied using a fixed-bed microreactor at atmospheric pressure with water as gasifying agent and calcined dolomite as catalyst. Working at temperatures in the range from 800 °C-900 °C lead to high gas yield with very small amount of liquid and solid residues. Good stability of dolomite catalysts was observed working at 900 °C during more than 60 hours tests. The water to wood ratio was found to affect markedly both gas amount and composition. Heating values in the range 2,500 kcal m⁻³-3,000 kcal m⁻³ were obtained for the different experimental conditions. A comparison of calcined dolomite with γ-alumina was afforded.

Biomass is a renewable source of fuels and chemicals and its utilization as a substitute of other fossil fuels is usually considered a valid alternative in the context of the policies for the implantation of new sustainable chemical processes [1, 2]. In addition, their utilization in many countries that do not dispose of their own resources of fossil fuels can also help to minimize the effect of foreign regulations imposed to imported fossil fuels.

In addition to the most traditional utilization of biomass residues by direct combustion, pyrolysis and gasification processes give place to upgraded gaseous, liquid and solid chemical compounds. In gasification processes, high gas yields are easily obtained by adjustment of the experimental conditions in order to favor cracking reactions of hemicellulose, cellulose and lignin fractions. Temperature values higher than 600 °C are usually employed for that purpose.

Different kind of catalysts can improve the gasification process in the following aspects:

- the amount of gases is increased through the enhancement of cracking reaction of liquid and solid products. At the same time the amount of liquid (tar) and solid (char) residues are greatly reduced;
- the gas composition can be adjusted according to the type of catalyst. A typical example is that of nickel-based catalysts which lead to gas mixtures with a very low hydrocarbons content.

Different earth-alkaline metal based minerals are reported as

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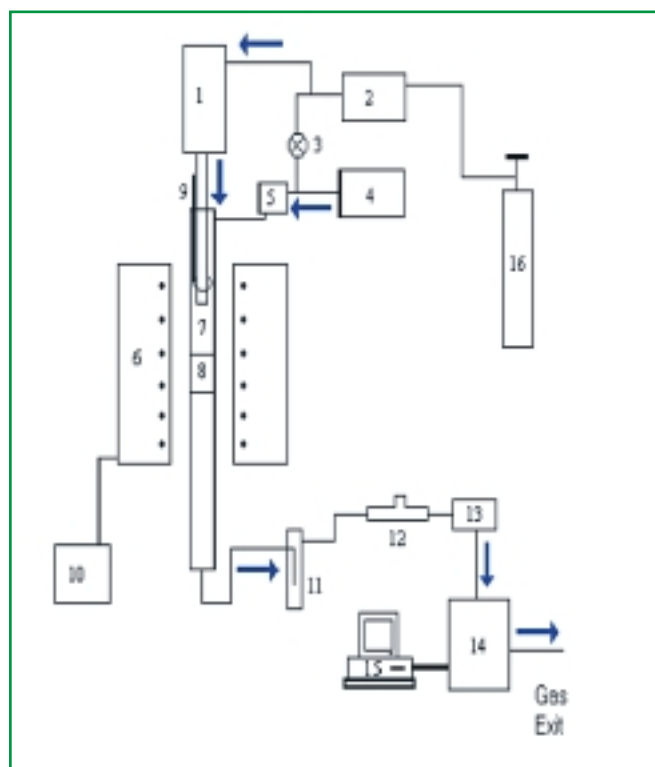
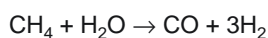


Figure 1 - Microreactor scheme: 1) sawdust feeder, 2) gas flow controller, 3) argon bypass, 4) liquid water injection pump, 5) gas heater, 6) tubular furnace, 7) gasification and catalytic reactor, 8) catalytic bed, 9) solids remover, 10) furnace temperature regulator, 11) cold trap, 12) tar and carbon filter, 13) gas flow meter, 14) gas chromatograph, 15) computer, 16) argon

low-cost precursors for gasification catalysts [3, 4]. In particular, dolomite (double calcium and magnesium carbonate) has been employed alone (one-stage process) [4-6] or combined with a second reforming catalyst such as nickel/alumina (two-stage process) [7-9]. When used alone, the main reaction products are hydrogen, carbon monoxide and carbon dioxide, together with small amounts (8%-14%) of light hydrocarbons such as methane, ethylene and propylene. In the second case, light hydrocarbons are almost completely eliminated because of their transformation through reforming reactions in the presence of water:



Dolomitic minerals can be found in our country and their choice seems to be reasonable as a first simple strategy for the development of biomass catalytic gasification processes. This paper reports the results of our studies on the catalytic gasification of wood residues of a fast-grow tree species (*Eu-*

Table 1 - BET surface area and total pore volume of the catalysts

Catalyst	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
Dolomite (= D)	19	0.32
Dolomite used 40 h	6	0.03
6.2%Ni/D	15	0.14
1.5%Ni/D	16	0.27
1.5%Ni/D used 60 h	7	0.06
Al ₂ O ₃ (= Al)	96	0.30
7.8%Ni/ Al ₂ O ₃	75	0.21
1.7%Ni/ Al ₂ O ₃	95	0.27

Table 2 - Composition of *Eucalyptus Camaldulensis* wood

Component	% Weight
Carbon	46.19
Oxygen	38.81
Hydrogen	4.89
Water	9.87
Ashes	0.24

calyptus camaldulensis) using a fixed-bed catalytic microreactor using calcined dolomite as catalyst. The influence of the principal process variables (temperature, amount of water in the feeding) on the gas amount and composition and on its heating value was investigated. The behavior of several kind of catalyst as well as their lifetime was compared.

Experimental

Dolomite (Ca=24.6%, Mg=19.7%, Fe 0.035% weight based) comes from Lavalleya at the middle-east region of Uruguay. Alumina catalysts were prepared with a commercial alumina Merck N° 1095 (>99.9 % Al₂O₃). Impregnation of dolomite and alumina was performed with aqueous solutions of nickel nitrate. For the impregnation of dolomite the mineral was previously decarbonated by heating at 900 °C, 3 hours in an argon stream. Then the nickel nitrate solution was introduced under vacuum by an incipient wetness method. Drying at 105 °C, 24 hours and calcination at 500 °C, 4 hours, were finally performed. A similar technique was employed for alumina-supported catalysts with exception of the calcination path. Catalysts were characterized by specific surface (Table 1), thermogravimetric analysis, X-ray diffraction before and after use. Characterization of *Eucalyptus* sawdust by elemental analysis, water content and ashes after calcination at 900 °C was performed (Table 2).

The gasification experiments were performed under atmospheric pressure with a fixed-bed microreactor shown in Figure 1. A SS 316 vertical tube (diameter=19 mm and length=700 mm) was used as reactor. A stainless steel grid was used to support the catalyst at the desired position into the tube. Sawdust enters the reactor at the top

and a home-made device assures a continuous feeding rate in the range of 2.5 g h⁻¹-5.0 g h⁻¹ with a reproducibility of 10%. Argon and water vapor are also fed at the top of the reactor. Water to sawdust feed ratio was adjusted for each experiment in the range from 0.4 to 2.8. The common experimental conditions used by us are the following: catalyst particles size=10-14 DIN, sawdust particle size=10-16 DIN, argon gas flow=2.7 l h⁻¹, sawdust feeding=3 g h⁻¹.

Gaseous products were analyzed by gas chromatography (Shimadzu GC-14B chromatograph) equipped with FID and TCD detectors. A Carbosieve S II packed column and argon as gas flow carrier were used.

Results and discussion

Definition of parameters for the gasification process:

Q_{p_m} = heating yield of the gas mixture in kcal kg⁻¹ wood;

Q_{p_v} = heating value of the gas mixture in kcal m⁻³ of gas;

V = volume of the gas mixture in l kg⁻¹ wood;

R = water vapor to sawdust feed ratio (g_{H₂O} h⁻¹)/(g_{wood} h⁻¹).

Table 3 shows the beneficial effect of the catalytic process. It can be seen that both the amount of gas products and their heating value are higher in the presence of a catalyst whereas a marked decrease of liquid and solid residues is also achieved.

Figure 2 shows the increase of the volume of gaseous products with the increase of temperature due to the higher rate of char gasification and hydrocarbons reforming reactions. The amount of hydrogen, carbon monoxide, carbon dioxide and methane increases strongly with the increase of the temperature. Contrarily, the amount of other reaction products such as ethylene and ethane diminishes at high temperatures due to cracking reactions. From thermogravimetric studies we know that recarbonation of dolomite takes place at temperatures lower than 800 °C. This recarbonation and coke deposits could be the reason for the lower temperature dependence of the catalytic activity observed in the range of temperatures between 500 °C and 700 °C. The heating value of the gaseous mixture gradually decreases from 3,650 kcal m⁻³ at 500 °C to 2,700 kcal m⁻³ at 900 °C. This is a consequence of the observed decrease of light hydrocarbons (C₂ and C₃) content due to higher rate of reforming reactions [10-12]. However, the heating yield (Q_{p_m}) increases from 970 kcal kg⁻¹ at 500 °C to 5,140 kcal kg⁻¹ at 900 °C mainly due to the increase of the volume of gaseous products.

In all the experiments solid residues (carbonaceous compounds and inorganic ashes) were found on the catalyst and the gasification zone. At low temperatures (500 °C-700 °C) they represent 20% of the fed wood whereas at higher temperatures (800 °C-900 °C) they are reduced to less than 5%. Colored condensed waters were also obtained at the exit of the reactor. They are not a very important amount but they

Table 3 - Influence of the utilization of a catalyst (calcined dolomite) in the gasification of *Eucalyptus* wood*

Run	Q_{p_m} (kcal kg ⁻¹ wood)	V (l kg ⁻¹ wood)	Q_{p_v} (kcal m ⁻³)	%Carbon
With catalyst	4,485	1,700	2,630	3.8
Without catalyst	3,125	1,250	2,495	9.3

*Catalyst mass=4 g (calcined dolomite), temperature=900 °C, R=1, time of the experiment=300 min.

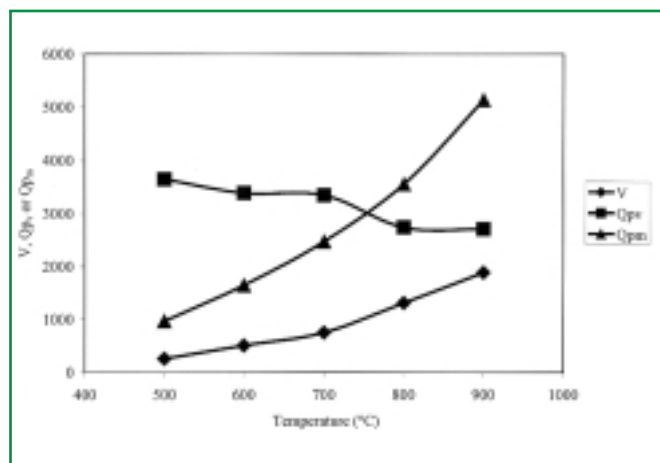


Figure 2 - Gas volume (liter kg⁻¹_{wood}), heating value of gases (kcal m⁻³) and heating yield (kcal kg⁻¹_{wood}). Influence of gasification temperature. Water/sawdust ratio=1; catalyst: calcined dolomite; mass of dolomite: 8 grams

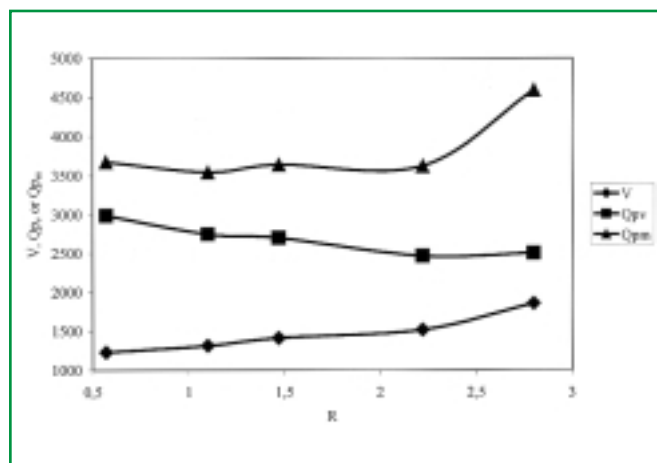


Figure 3 - Gas volume (l kg⁻¹_{wood}), heating value of gases (kcal m⁻³) and heating yield (kcal kg⁻¹_{wood}). Influence of the water/sawdust ratio. Gasification temperature: 800 °C; catalyst: calcined dolomite; mass of dolomite: 8 grams

gradually disappear with the increase of the gasification temperature.

Experiments performed with different dolomite weight to sawdust flow rate ratio in the range 1.33-5.33 show small changes (less than 10%) in the evaluated parameters.

Figure 3 shows the influence of the water to biomass ratio (R) on the gasification process. The volume of gases gradually increases from 1,230 l kg⁻¹_{wood} at R=0.57 to 1,860 l kg⁻¹_{wood} at R=2.80. This can be explained by the higher rate of char gasification and hydrocarbon reforming reactions.

The increase of hydrogen and carbon dioxide, the decrease of carbon monoxide and the decrease of Q_{pv} can be explained by the displacement of the water-gas shift reaction equilibrium ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) to the right side. The amount of methane and other light hydrocarbons is not significantly affected by the change of R.

The comparison of dolomite with γ -alumina shows very similar results (Table 4). Contrarily the nickel-loaded catalysts led to a significant increase in the gas volume. The heating value was lower for the loaded catalysts due mainly to the disappearance of light hydrocarbons. All these features clearly demonstrate the well known properties of nickel as a reforming catalyst [7-9]. We could also observe the beneficial effect of nickel for the reduction of the condensed products. A significant reduction in the amount of gas products took place with the increase of the amount of loaded metal for both dolomite and alumina supported catalysts. This behavior can be ex-

plained by the corresponding differences in surface specific area (Table 1) and probably to a more important formation of carbon deposits.

In a previous work the aging of catalysts was monitored: dolomite and 1.5% Ni/dolomite, at 900 °C and 60 hour tests [13]. For both catalysts a gradual increase of the gas formation was observed until about 7 hours. The gas volume values were stabilized at 1,200 l kg⁻¹ and 1,500 l kg⁻¹ for dolomite and Ni/dolomite respectively.

During the initial reaction period the total amount of carbonaceous residues rapidly increased and reached an almost constant value (0.5 g), which remains unchanged until the end of the experiments. The increasing contribution of these residues to the gas product formation can explain the observed behavior. The heating value also increased during the first 4 hours as a consequence of the change in the gas composition. Indeed, high reforming activity takes place with the fresh decarbonated catalyst which led to an initial low hydrocarbons content. After 8 hours the heating value remained in an almost unchanged value until the end of the experiment (2,900 kcal m⁻³ and 2,700 kcal m⁻³ for the dolomite and Ni/dolomite respectively).

The effect of the different experimental conditions (temperature, R, type of catalyst) in the H₂/CO ratio shows several important aspects. For a dolomite catalyst, at R=1, the H₂/CO ratio changes with temperature, passing from 0.4 at 500 °C to 2.0 at 900 °C. For the same catalyst and at 800 °C, the

Table 4 - Experiments with different catalysts*

Catalyst	H ₂ (mol min. ⁻¹)x10 ⁴	CO	CO ₂ (l kg ⁻¹ _{wood})	CH ₄ (kcal m ⁻³)	C ₂ **	H ₂ /CO	V	Q _{pv}
Dolomite (= D)	10.5	5.3	2.2	2.5	0.16	2.0	1,080	3,010
1.5%Ni/D	14.5	11.2	2.2	1.7	0.02	1.3	1,540	2,660
6.2%Ni/D	11.8	8.5	0.7	1.3	0	1.4	1,230	2,740
Al ₂ O ₃ (= Al)	9.5	4.0	2.5	2.3	0.18	1.8	1,100	3,060
1.7%Ni/Al	17.9	12.0	3.2	1.7	0	1.5	1,920	2,510
7.8%Ni/Al	13.8	9.7	0.4	0.6	0	1.4	1,340	2,620

*Catalyst mass=4 g, feeding flow rate=45 mg min.⁻¹ (dry basis), temperature=900 °C, R= 0.4, time of the experiment=300 min.; **C₂=C₂H₄ + C₂H₆

H₂/CO ratio changes strongly with the change of R (for R=0.57, H₂/CO=2.1 and for R=2.8, H₂/CO=5.3). The nickel loaded catalysts lead to lower H₂/CO ratios (Table 4).

Conclusions

All these studies show the validity of the results obtained in a microscale gasification for the study of the influence of different parameter affecting the catalytic gasification process.

Indeed our results are in good agreement with those obtained for other authors confirming the good properties of dolomite as a biomass gasification catalyst. The gas heating value obtained with Eucalyptus sawdust (Q_p, about 3,000 kcal m⁻³) is similar to that obtained for other kind of wood species reported in the literature. The gas mixture is suitable for fuel utilization and due to the high content in hydrogen and carbon monoxide, it could also be used for organic compounds synthesis and hydrogenation reactions.

The comparison of dolomite with other typical solid material such as alumina does not show significant differences in the catalytic activity. This is an important feature taking account of the low-cost and high availability of these mineral resources in our country.

The impregnation of catalysts (dolomite and alumina) with nickel shows that secondary liquid and solid residues can be reduced as well as light hydrocarbons. By this way much more pure gaseous mixtures can be obtained for the purposes of their utilization in synthesis or hydrogenation application. In addition, higher gas volumes are obtained (1,500-2,000 l kg⁻¹_{wood}) with almost the same heat value (2,500-3,000 kcal m⁻³). Small proportion of nickel seems to be more effective for the enhancement of the catalytic activity.

Very small deactivation of dolomite catalyst at 900 °C is also an important aspect to be remarked in order to be used in industrial biomass gasification processes.

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