Pyrolysis of Sawdust in a Conical Spouted-Bed Reactor with a HZSM-5 Catalyst

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The effect was studied of using in-situ catalyst based on a HZSM-5 zeolite in flash pyrolysis with an inert gas (N_2) *of sawdust of pinus insignis in a conical spouted-bed reactor in the* $400-500°C$ *range and for a gas residence time of 50 ms. The use of the catalyst increases the yield of gases and decreases the yields of liquid and char. Likewise, the yield of* CO_2 *decreases, whereas the yield of* C_{4-} *hydrocarbons increases (15.9 wt. % at 450°C). The catalyst is efficient for partial deoxygenation of the liquid product.*

Introduction

Flash pyrolysis is one of the routes that provides enhanced prospects for large-scale exploitation of biomass material (Bridgwater and Bridge, 1991; Bridgwater and Cottam, 1992). The fluidized bed is the more developed technology (Scott and Piskorz, 1984a, b; Scott et al., 1988; Samolada and Vasalos, 1991; Liden et al., 1988; Bilbao et al., 1988; Stiles and Kandiyoti, 1989; Font et al., 1986, 1990; Arauzo et al., 1997), although other reactors have been proposed, such as the transport reactor (Gorton et al., 1990; Fjellerup et al., 1996), cyclonic reactor (Choi, 1978), impinging-stream reactor (Berg et al., 1989), and rotating-cone reactor (Waagenar et al., 1994).

The conical spouted-bed reactor is an interesting alternative due to the fact that its versatility in gas flow allows for handling solids that, like biomass, have an irregular texture, without using another inert solid in order to attain biomass cyclic movement (Olazar et al., 1994). Due to the vigorous gas–solid contact corresponding to the regime of transition between the regimes of spouted bed and jet spouted bed, suitable conditions for obtaining a high yield of liquid product are reached: high biomass heating rate, short residence time of gaseous products in the reactor, and temperature uniformity in the reactor. This performance gives way to a reduction in energy consumption and allows for obtaining a liquid product of standard composition as a consequence of the minimization of the secondary reactions, undergone by the pyrolysis products. It has been proven that this technology allows for obtaining similar liquid product yields as in fluidized beds, and that the liquid is also of similar composition (Aguado, 1999; Aguado et al., 1999).

The liquid product obtained by flash pyrolysis is highly oxygenated and arouses great interest due to its heat value (16–18 MJ kg^{-1}), ease of handling, and the interest of its individual components. Bearing in mind present aspirations, which mainly lie in its use as fuel, the goal is to improve the quality of pyrolysis liquid product and to achieve a liquid fuel with a composition similar to that of a conventional fuel.

Upgrading the liquid product obtained by flash pyrolysis (with an approximate empirical formula $C_6H_8O_4$) consists of deoxygenation and decarboxylation in order to reduce the content of oxygen and the C/H ratio, and obtain a more stable, homogeneous, and less corrosive liquid product. The more interesting routes are catalytic transformations, either by hydrodeoxygenation (HDO) or by direct transformation (dehydration and cracking). Reviews of these methods have appeared in the literature (Elliott et al., 1991; Bridgwater and Cottam, 1992; Bridgwater, 1994).

In view of the high hydrogen consumption and the high catalyst/feed ratio required for complete hydrodeoxygenation (Sheu et al., 1988), the interest is directed toward partial deoxygenation, with the aim of attaining a stable liquid product that is suitable for turbine feed (Laurent et al., 1994).

Catalytic transformation of pyrolysis liquid product in a different reactor to that used for the pyrolysis process is an alternative supported by the interest in operating under at-

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mospheric pressure and without feeding H_2 and has been studied in the literature, mainly by using HZSM-5 zeolites (Chen et al., 1988; Adjaye and Bakhshi, 1994; Katikaneni et al., 1995). It is well known that the HZSM-5 zeolite is able to transform both pure light oxygenates (ethanol, propanol, butanol, acetic acid, acetone etc.) and their mixtures into liquid hydrocarbons and olefins (Chang and Silvestri, 1977; Derouane et al., 1978). Likewise, the ability of HZSM-5 zeolite also has been proven for the transformation into hydrocarbons of the biomass constituents of high molecular weight (rubber latex, vegetable oils or extracts of these oils, and residual oils) (Weisz et al., 1979; Prasad and Bakhshi, 1986; Milne et al., 1990; Sharma and Bakhshi, 1991a).

Direct transformation of the gaseous stream coming from the pyrolysis reactor has also been studied (Evans and Milne, 1987; Diebold and Scahill, 1988). This transformation avoids liquid-product instability problems, as well as becoming uncontrolled when heated to the reaction temperature.

The results of catalytic transformation on HZSM-5 zeolites in the literature are hardly comparable because in many cases the liquid product used as feed was not obtained by pyrolysis but by extraction (Chantal et al., 1984; Costa et al., 1991) or by liquefaction of wood (Mathews et al., 1985; Sharma and Bakhshi, 1991b, 1993a; Adjaye and Bakhshi, 1995). On the other hand, when the liquid comes from a pyrolysis unit, the operating conditions of the units (pressure and temperature) may have been very different, which affects liquid composition (Evans and Milne, 1987; Renaud et al., 1988; Diebold and Scahill, 1988).

Other acid catalysts have also been tried: silica-alumina, HY zeolite, H-mordenite, silicalite, silicoaluminophosphates, and MgAPO-36 (Adjaye and Bakhshi, 1994; Katikaneni et al., 1995), but their application is subject to greater uncertainties than with HZSM-5 zeolite.

In this article, the use of a catalyst *in situ* within the pyrolysis reactor is proposed in order to compare both yields and composition of the products with those obtained by pyrolysis without catalyst. Pyrolysis with catalysts has already been approached by means of hydrodeoxygenation catalysts and a high yield of gases has been obtained (Arauzo et al., 1994, 1997). The reactor used in this article is a conical spouted-bed reactor, which is especially suitable for this strategy because, as it does not require any inert material, the amount of catalyst may be used as the variable for controlling product composition. The low segregation observed in spouted beds, which also has been proven in conical spouted beds (San José et al., 1994), is an advantage over the fluidized bed. Moreover, the pyrolysis temperature in these contactors (below 500°C) is suitable for the high activity of the HZSM-5 zeolite.

Experimental Studies

Pyrolysis equipment

The laboratory unit (Figure 1) consists of the following components (Aguado, 1999; Aguado et al., 1999): solid feeder; device for feeding inert gas; the pyrolysis reactor; condensation system; device for char quenching and extraction; section for on-line gas analysis.

The reactor, which is shown in Figure 2, has a conical shape and is provided with an upper cylindrical section. The geometric factors of the reactor are total reactor height, $H_T = 34$ cm; height of the conical section, $H_c = 20.5$ cm; angle of the conical section, $\gamma = 28°$; diameter of the cylindrical section, $D_c = 12.3$ cm; base diameter, $D_i = 2$ cm; inlet diameter, $D_o = 1$ cm. The hydrodynamics and design factors of the conical spouted beds have been studied in previous articles (Olazar et al., 1992; 1993; San José et al., 1993).

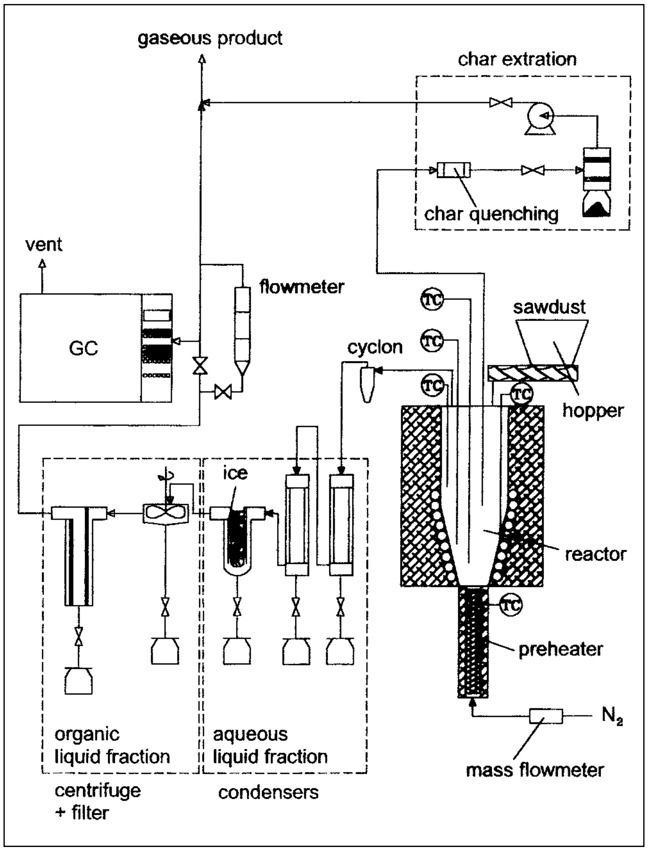

Figure 1. Pyrolysis plant.

Nitrogen is fed through the bottom of the reactor once it has been heated by direct contact with resistances inserted into the ceramic material and covered with a metallic case. Another resistance inserted into the ceramic material covers the conical section of the reactor and maintains the wall temperature. The reactor and the upper cylindrical section are insulated. The gas inlet temperature and the wall temperature are controlled by means of two fixed thermocouples. Furthermore, there are another three thermocouples, which are located at three radial locations and are provided with free vertical movement.

Condensation of the gaseous stream is carried out by means of a system consisting of condensers−centrifuge−filter arranged in series. An aqueous fraction condenses in the first section of the system, which consists of two coils cooled by water and a trap refrigerated by ice. Subsequently, in order to retain the entire organic fraction, the gaseous stream is passed through a 10,000-rpm centrifuge and then through a 25-μm sintered steel filter. The organic fraction retained in the filter is recovered by washing with acetone (whose quantity is approximately 50 wt. % of the liquid retained), followed by vacuum distillation. A bubble flow-meter is placed at the exit of the filter to measure the gaseous-stream flow

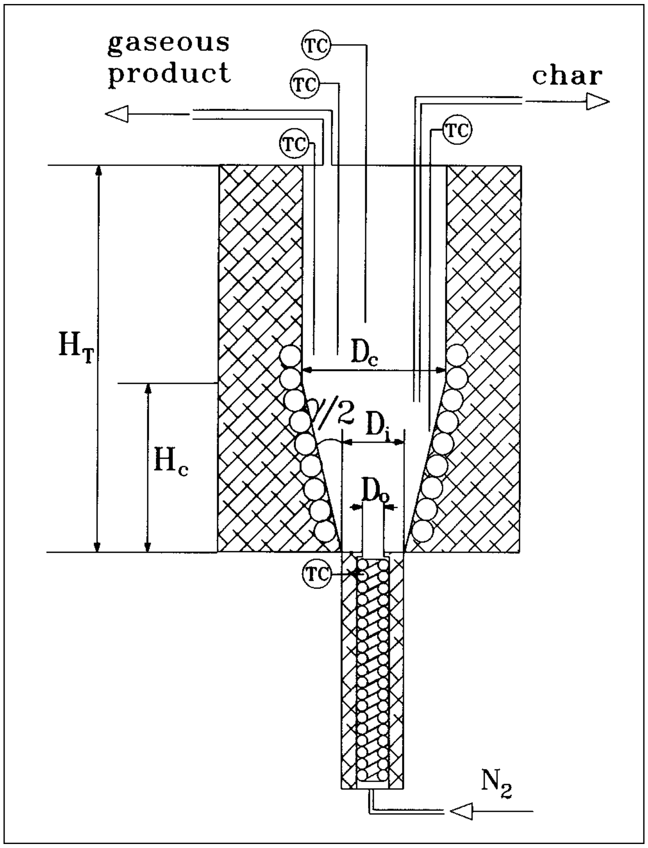

Figure 2. Pyrolysis reactor.

rate. The composition of the departing gases is analyzed by gas chromatography (Hewlett-Packard 5890 II).

Char extraction is facilitated by a solid flow pattern (Olazar et al., 1996; San José et al., 1998) and segregation in the conical spouted beds (San José et al., 1994) and is carried out by turning on a suction pump connected to a pipe, which is lowered into the reactor to a variable level in the annular zone (solid descending zone) of the bed. Char extraction is controlled, and so the bed height is maintained at a given value, by means of two independent devices, the first activated by a pressure increase in a small nitrogen stream continuously passing through the char extraction pipe, the second as pressure drop in the bed increases.

Operating conditions

The runs have been carried out by continuously feeding sawdust under the following conditions: biomass, pine sawdust (at equilibrium humidity at room temperature) with a particle size between 0.8 and 2.0 mm; sawdust flow, between 2 and 6 g min^{-1}; catalyst (10 g), with a particle size between 0.7 and 1.35 mm; temperature, 400°, 450°, and 500°C; N_2 flow rate, 20% over that of the minimum spouting velocity, within the 10−14 = L min^{-1} range, depending on temperature; time between char extractions, 8−10 min; run length 5 h. The bed regime corresponds to a transition state close to the regime of the spouted bed. Under these conditions, the average residence time of the gas (nitrogen) in the bed is 50 ms, and for the gas that circulates along the spout zone (approximately 60% of the total flow), the residence time is approximately 20 ms. The upper temperature limit is 500°C in order to avoid irreversible deactivation of the catalyst by dealumination.

From the proximate analysis of the sawdust, carried out by thermogravimetry (Setaram TAG 24), the following results (in wt. %) have been obtained: fixed carbon, 16.04; volatile matter, 83.74; ash, 0.22. The results of the final analysis (Perkin-Elmer 2400CHN) are (in wt. %) C, 44.80; H, 6.56; N, 0.05, O, 48.49; S, 0.1.

Product characterization

The analysis of the gaseous stream is carried out by a gas chromatograph (Hewlett-Packard 5890 II), along with a TCD detector, Porapak Q column, 6-way pneumatic valve, and molecular sieve.

The aqueous and organic fractions of the liquid have been analyzed by GC/MS in equipment consisting of a Hewlett-Packard 5890 II gas chromatograph, along with a BPX5 capillary column (nonpolar) of 50 m and a Hewlett-Packard 5989B mass spectrometer connected on-line. The peaks have been identified by means of the WILEY 6N library. While the aqueous fraction may be injected as it is, the organic fraction must be dissolved in acetone. The water content in the aqueous fraction has been determined by Karl Fischer (Rapid Test, Merck).

Catalyst

The preparation method (Argauer and Landolt, 1972 consists of obtaining an active HZSM-5 zeolite (Si/AI = 24), which, once mixed with a suitable binder (bentonite from Exaloid) and an inert charge (fused alumina from Martinswerk), is subjected to wet extrusion in order to acquire the proper shape and handling conditions. The catalyst has been equilibrated by thermal treatment (calcination in a N_2 stream at 570°C). Once the HZSM-5 zeolite is subjected to these conditions, it is not dealuminated in a reaction medium with high water content at temperatures below 500°C (Sano et al., 1996; Benito et al., 1996a). On the other hand, below 500°C, water attenuates deactivation by coke mainly in the MTG process and, moreover, favors selectivity to light products (Aguayo et al., 1997).

The physical properties of the HZSM-5 zeolite and the catalyst, which have been determined by N_2 adsorption−desorption in an ASAP 2000 surface analyzer from Micromeritics, are contained in Table 1. The values of the zeolite crystal size have been determined in a Coulter Mastersizer, and the degree of crystallinity has been measured by FTIR in a Nicolet 740 spectrophotometer, from the intensity ratio of the bands at 550 and 450 cm^{-1}.

The results of the chemical adsorption of NH_3 at 250°C obtained by differential scanning calorimetry (Gayubo et al., 1996) (Figure 3) show that the total acidity is 0.50 (mmol of NH_3) g^{-1} and that the distribution of acidity strength of the sites is relatively wide. Half of the sites are strong, as an adsorption heat higher than 150 kJ (mol of $NH_3)^{-1}$ is released, whereas the remaining sites are moderately acid, as their adsorption heat is between 130 and 150 kJ (mol of $NH_3)^{-1}$.

Table 1. Properties of the HZSM-5 Zeolite and the Catalyst

Properties of the HZSM-5 Zeolite				
BET Area ($m^2 \cdot g^{-1}$)	Pore Vol. $cm^3 \cdot g^{-1}$	Density ($g\ cm^{-3}$)	Crystall. (%)	Crystal Size (μm)
420	0.65	0.94	93	3.6
Pore-Volume Distribution of the Catalyst				
% Micropore $d_p < 10^{-3}\ \mu m$	% Mesopore $10^{-3}\ \mu m < d_p < 0.01\ \mu m$	%Macropore $0.01\ \mu m < d_p < 2\ \mu m$		
8.0	14.7	77.2		
Physical Properties of the Catalyst				
BET Area ($m^2 \cdot g^{-1}$)	Pore Volume ($cm^3 \cdot g^{-1}$)	Particle Density ($g \cdot cm^{-3}$)	Solid Density ($g \cdot cm^{-3}$)	
124	0.433	1.21	2.53	

The ratio between Bronsted/Lewis acid sites is 2.86, which was determined from the intensity ratio of the IR bands at 1,550 and 1,450 cm^{-1} once pyridine was adsorbed.

Results

Yields

In Figure 4 the gas, liquid, and char yields obtained with and without catalyst are compared. It is observed that using the catalyst at 400°C the yield of gases increases from 11.2 to 23.5 wt.% and that this effect of the catalyst weakens as temperature is increased.

In the runs with catalyst, a noticeable decrease in the yield of liquid is observed. Maximum yield is obtained at the lowest temperature studied (400°C), while it is constant up to 450°C and then drops at 500°C.

The yield of char at 400°C is appreciably lower when the catalyst is used (from 21.5 to 16.5 wt.%), but this decrease attenuates as temperature is increased.

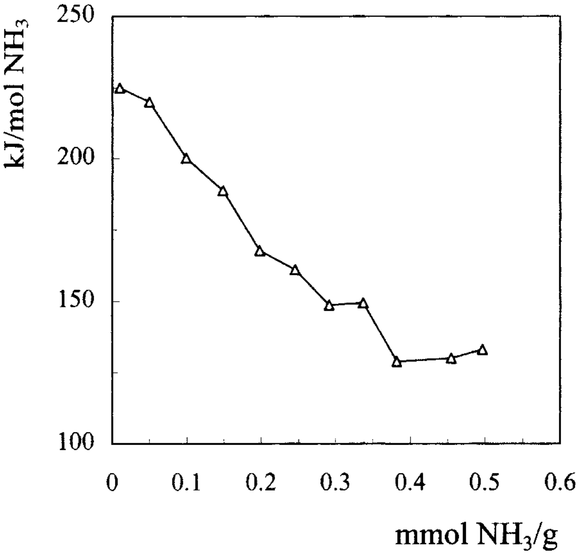

Figure 3. Results of differential NH_3 adsorption on the catalyst by calorimetry.

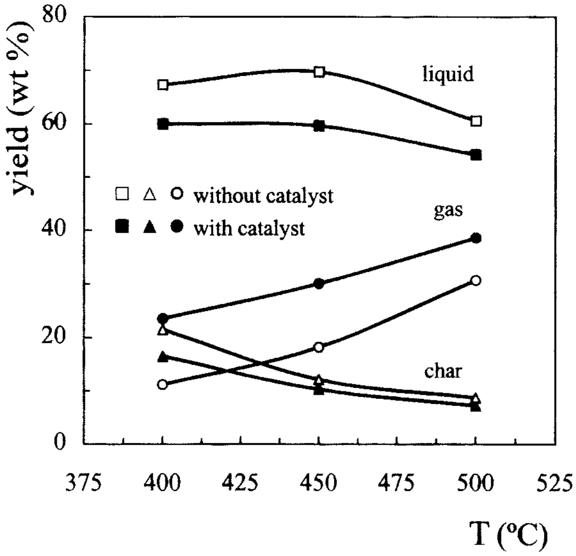

Figure 4. Effect of the catalyst on the distribution of products in the pyrolysis of sawdust at different temperatures.

The catalyst effect on liquid product distribution, that is, on the amount of aqueous and organic fractions, is analyzed in Figure 5. It is seen that the organic fraction decreases in a very pronounced way, with the larger decease at 400°C (from 42.6 to 20.2 wt.%), and it then attenuates as the temperature is increased. On the other hand, the yield of the aqueous fraction increases with the catalyst. This increase is more important at 400°C (from 24.7 to 39.8 wt.%) and attenuates as temperature is increased.

Nevertheless, this increase in the aqueous-fraction yield may give way to confusion if the increase in water content in

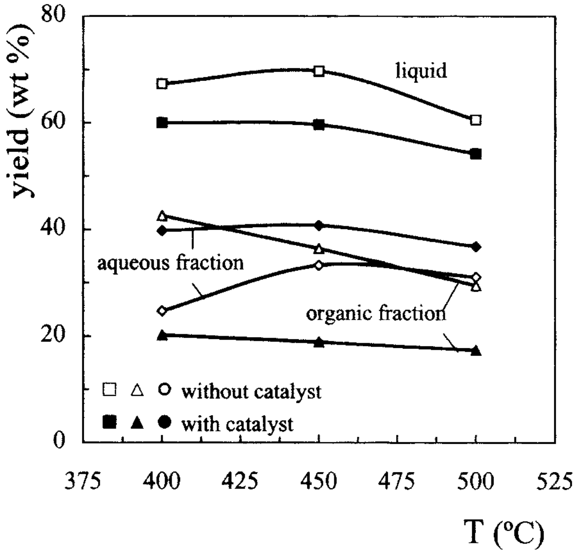

Figure 5. Effect of the catalyst on the distribution of both liquid fractions in the pyrolysis of sawdust at different temperatures.

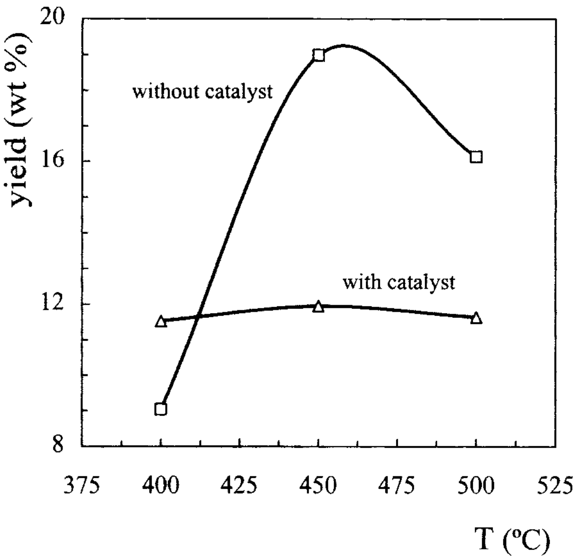

Figure 6. Effect of the catalyst on the yield of organic compounds in the aqueous-liquid fraction of pyrolysis.

this fraction is not taken into account. Once this aspect is considered, as Figure 6 shows, the catalyst effect on the yield of the organic compounds is visible in the aqueous liquid fraction. It is observed that at 450° and 500°C there is an important decrease in the yield of organic compounds when the catalyst is used, which means that at these temperatures the catalyst favors the transformation of these organic compounds from the aqueous fraction to gases, instead of their formation from the organic liquid fraction. On the other hand, at 400°C, the yield of the organic compounds in the aqueous fraction is higher when the catalyst is used, because at this temperature cracking of organic compounds in the liquid fraction is favored. It is noteworthy that as a result of the formation and disappearance reactions, the yield of the organic compounds in the aqueous fraction when the catalyst is used is almost independent of reaction temperature in the 400–500°C range. Consequently, the catalyzed reaction steps are secondary ones and they explain the aforementioned yields. In Figure 7, the primary steps of thermal pyrolysis established by Shafizadeh (1975) for biomass pyrolysis have been indicated by single lines and the secondary catalyzed reaction steps have been indicated by double lines.

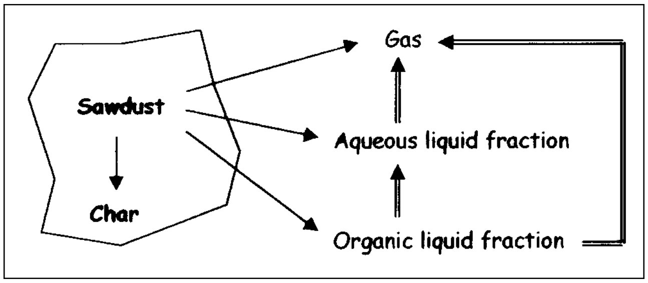

Figure 7. Steps for pyrolysis with HZSM-5 zeolite.

Single lines: thermal pyrolysis steps. Double lines: catalyzed reaction steps.

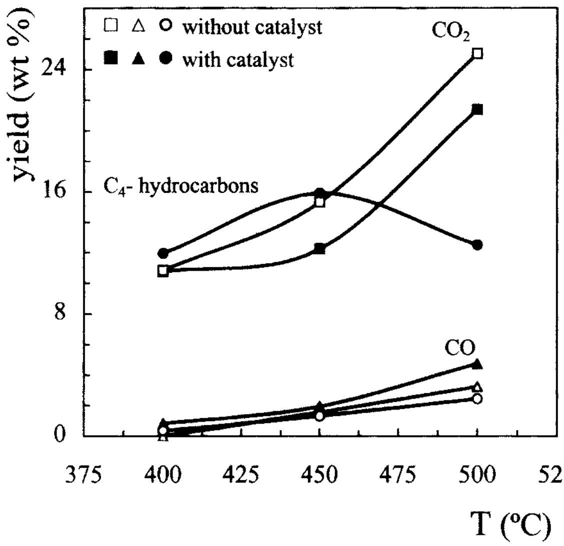

Figure 8. Effect of the catalyst on the distribution of pyrolysis gases.

Product composition

Analyzing the effect of using the catalyst on gas composition (Figure 8), and important increase in C_{4-} hydrocarbons is observed, whose maximum yield (15.9 wt.%) is reached at 450°C. As the temperature is increased to 500°C, the yield of C_{4-} hydrocarbons appreciably decreases and the yield of CO_2 greatly increases (from 12.2 to 21.4 wt%).

The yields of each one of the compounds in the C_{4-} fraction and of CO and CO_2 are presented in Table 2. A high yield of ethylene (8.9 wt. %) and of methane (5.8 wt. %) at 450°C is noteworthy. As the temperature is increased, the yield of CO increases, but the yield of CO_2 does so in a more pronounced way. In this sense, the important role played by the catalyst in reducing CO_2 production at temperatures above 400°C, and particularly at 450°C (from 15.31 to 12.23 wt. %), is noteworthy, although the yield of CO is slightly higher when the catalyst is used (1.94 as against 1.55 wt. %).

Figure 9 shows the distribution of compound families in the aqueous liquid fraction obtained by catalytic pyrolysis. The knowledge of this composition is interesting in view of a subsequent upgrading by catalytic transformation in another reactor using suitable catalyst and reaction conditions.

The values of Figure 9, together with those corresponding to noncatalytic pyrolysis, are contained in Table 3. When both

Table 2. Yields of the Compounds in the Pyrolysis Gases, wt. %

	Without Catalyst			With Catalyst		
	400°C	450°C	500°C	400°C	450°C	500°C
Methane	0.00	0.00	0.00	5.66	5.80	3.36
Ethene	0.00	0.02	0.12	5.44	8.89	5.96
Ethane	0.00	0.00	0.02	0.00	0.08	0.30
Propene	0.00	0.00	0.41	0.00	0.00	0.56
Propane	0.00	0.00	0.12	0.00	0.00	0.21
n-Butane	0.30	1.18	1.59	0.44	0.44	0.93
i-Butane	0.05	0.11	0.19	0.39	0.67	1.17
CO	0.00	1.55	3.24	0.82	1.94	4.74
CO_2	10.83	15.31	25.02	10.74	12.23	21.36

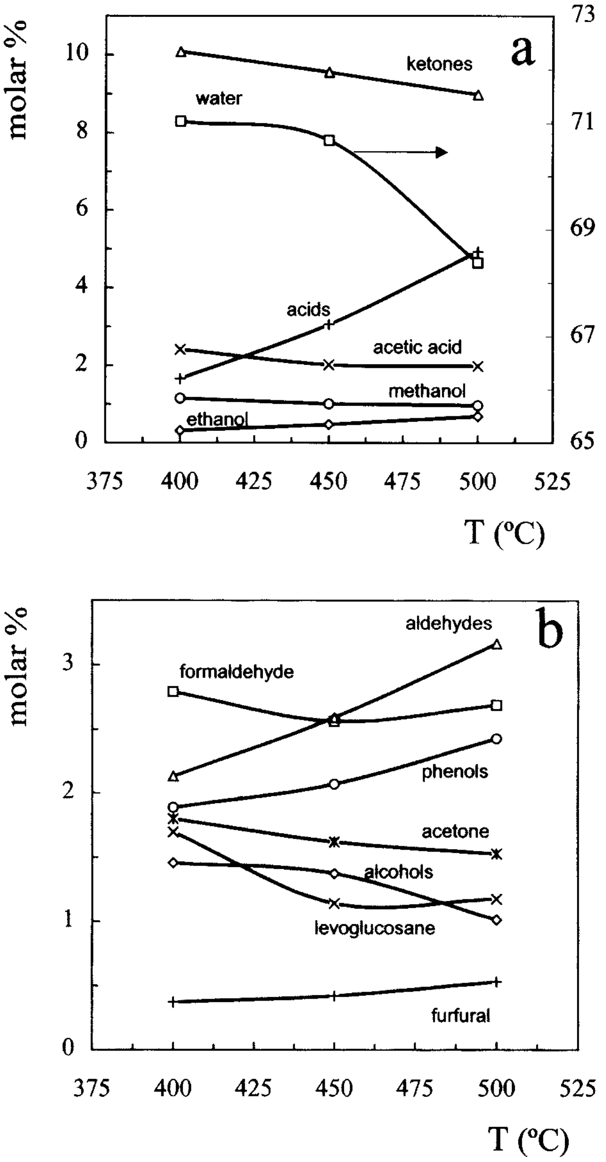

Figure 9. Distribution by families of the aqueous liquid fraction of catalytic pyrolysis.

Table 3. Composition (by Families), Molar %, of the Aqueous Fraction of Pyrolysis

	Without Catalyst			With Catalyst		
	400°C	450°C	500°C	400°C	450°C	500°C
Water	63.40	43.00	48.10	71.03	70.68	68.38
Formaldehyde	2.47	3.64	4.09	2.79	2.56	2.69
Methanol	2.64	2.68	2.49	1.15	1.01	0.97
Ethanol	0.05	0.12	0.32	0.32	0.48	0.68
Acetic Acid	3.24	5.34	4.80	2.42	2.02	1.98
2-Butanone	1.80	3.32	2.58	1.80	1.62	1.53
Furfural	0.52	1.00	0.68	0.37	0.42	0.53
Levoglucosane	0.84	2.07	2.31	1.70	1.14	1.18
Ketones	10.40	15.70	14.27	10.08	9.56	8.98
Aldehydes	3.20	4.18	4.29	2.13	2.59	3.17
Alcohols	1.91	2.96	3.14	1.46	1.37	1.01
Acids	5.19	7.96	6.68	1.66	3.06	4.93
Phenols	3.39	6.69	5.23	1.89	2.07	2.43
Other	0.95	1.34	1.02	1.20	1.42	1.54

compositions are compared, it can be seen that, in addition to an increase in water content in the liquid obtained by catalytic pyrolysis, there is a general decrease in composition of almost all the compounds except ethanol. On the other hand, while the composition of the organic compounds in the noncatalytic pyrolysis liquid increases with temperature, which is a consequence of a decrease in water content, in the catalytic pyrolysis liquid the composition hardly changes in the temperature range studied, because the water content hardly changes with temperature.

According to the scheme in Figure 7, the lower hydrocarbon content when the catalyst is used is a consequence of a negative net yield as far as their formation and transformation to gases by dehydration and/or cracking are concerned. The result obtained for ethanol, for which the composition is noticeably higher in the catalytic pyrolysis liquid, can be explained by the following two aspects: (1) a positive balance for its formation from the organic liquid fraction; and (2) transformation into ethylene by dehydration also occurs in the noncatalytic pyrolysis, where the surface of the sand used as inert is sufficient for thermal dehydration of ethanol. Nevertheless, when the catalyst is used, the other reactants also compete for active sites, and consequently the catalyst surface area is less efficient for ethanol dehydration.

The yields, in wt. %, of each of the families into which the compounds of the aqueous liquid fraction have been grouped are compared in Table 4. It can be seen that, from the organic compounds, the yields of methanol, levoglucosane, alcohols, acids, and phenols are the ones most affected by the use of the catalyst from 450°C onwards.

As an example of the results observed at the three temperatures studied, the compositions, in mol %, and the yields, in wt. %, of each of the families that made up the organic fraction of the pyrolysis liquid obtained at 500°C are compared in Table 5. It can be seen that the catalyst affects all the families (except aldehydes) and especially phenols, where catalyst influence is significant, as is inferred from the magnitude of the yield of these compounds.

The use of the catalyst produces an important yield (8.2 wt. %) of nonoxygenate hydrocarbons within the C_5–C_{10} range, which, due to their high octane number, are potentially inter-

Table 4. Yields of Compound Families in the Aqueous-Liquid Fraction of Pyrolysis, Wt. %

	Without Catalyst			With Catalyst		
	400°C	450°C	500°C	400°C	450°C	500°C
Water	15.66	14.32	14.96	28.27	28.80	25.16
Formaldehyde	0.61	1.21	1.27	1.11	1.04	0.99
Methanol	0.65	0.89	0.77	0.46	0.41	0.36
Ethanol	0.01	0.04	0.10	0.13	0.20	0.25
Acetic Acid	0.80	1.78	1.49	0.96	0.82	0.73
2-Butanone	0.44	1.11	0.80	0.72	0.66	0.56
Furfural	0.13	0.33	0.21	0.15	0.17	0.20
Levoglucosane	0.21	0.69	0.72	0.68	0.46	0.43
Ketones	2.57	5.23	4.44	4.01	3.90	3.31
Aldehydes	0.79	1.39	1.33	0.85	1.06	1.17
Alcohols	0.47	0.99	0.98	0.58	0.56	0.37
Acids	1.28	2.65	2.08	0.66	1.25	1.81
Phenols	0.84	2.23	1.63	0.75	0.84	0.89
Other	0.23	0.45	0.32	0.48	0.58	0.57

Table 5. Composition of the Organic-Liquid Fraction of Pyrolysis, Molar %, and Yields of Compound Families, wt. % at 500°C

	Without Catalyst		With Catalyst	
	Composition	Yield	Composition	Yield
Furfural	1.1	0.32	1.0	0.18
Levoglucosane	12.3	3.63	6.2	1.08
Ketones	18.8	5.55	11.1	1.94
Aldehydes	7.2	2.12	11.7	2.03
Alcohols	10.6	3.13	3.2	0.56
Acids	1.8	0.53	0.9	0.15
Phenols	46.4	13.69	17.5	3.05
Other	1.8	0.50	1.2	0.21
Nonoxygenate (C_5-C_{10})	—	—	*47.2*	*8.20*
Aromatics	—	—	36.3	6.31
Benzene	—	—	3.3	0.57
Methylbenzene	—	—	15.6	2.71
Ethylbenzene	—	—	2.9	0.50
Xylenes	—	—	12.3	2.15
C_9-C_{10}	—	—	2.2	0.38
Paraffins	—	—	7.6	1.32
Olefins	—	—	3.3	0.57

esting as fuel. Most of them are aromatic hydrocarbons (yield of 6.3 wt. %), which, arranged in order from high to low content, are methylbenzene, xylenes, benzene, ethylbenzene, and heavier ones. The nonaromatic hydrocarbons are mainly paraffins and, to a lesser extent, olefins.

Because the main feature of this article is the use of an HZSM-5 zeolite in the pyrolysis process itself, we cannot carry out a precise comparison of the present results with those obtained in the literature by transforming the liquid product in a subsequent reaction step. As far as the yield of the C_5-C_{10} fraction is concerned, it is very similar to that obtained by Chantal et al. (1984) and Sharma and Bakhshi (1991b). Diebold and Scahill (1988) also observe the important presence of methylbenzenes. It is noteworthy that the integration of the catalytic process into the pyrolysis process avoids the transformation undergone by the liquid product due to the evaporation and subsequent heating to the reaction temperature in the second unit. This explains why coke formation on the catalyst is not qualitatively higher than that observed in the transformation of methanol under similar temperature conditions and water concentration in the reaction medium (Benito et al., 1996b). In fact, the presence of water in the reaction medium is a very important factor for attenuation of coke deactivation (Aguayo et al., 1997), although its effect on deactivation by catalyst dealumination must be studied in more detail.

Other factors that are different between the experimental system of this article and those of the literature are the nature of the raw material and the conditions used for catalytic transformation. Thus, the liquid product used as raw material in certain studies was obtained by supercritical extraction with methanol (Chantal et al., 1984) and by liquefaction (Mathews et al., 1985; Sharma and Bakhshi, 1991b), so its composition is different in certain aspects, such as the content of polynuclear aromatics, which seriously affect the catalytic behavior of the HZSM-5 zeolite. Mathews et al. (1985) have observed the higher yield of aromatics in the catalytic transformation of a small fraction of the raw material, which vaporizes in the 60–150°C range.

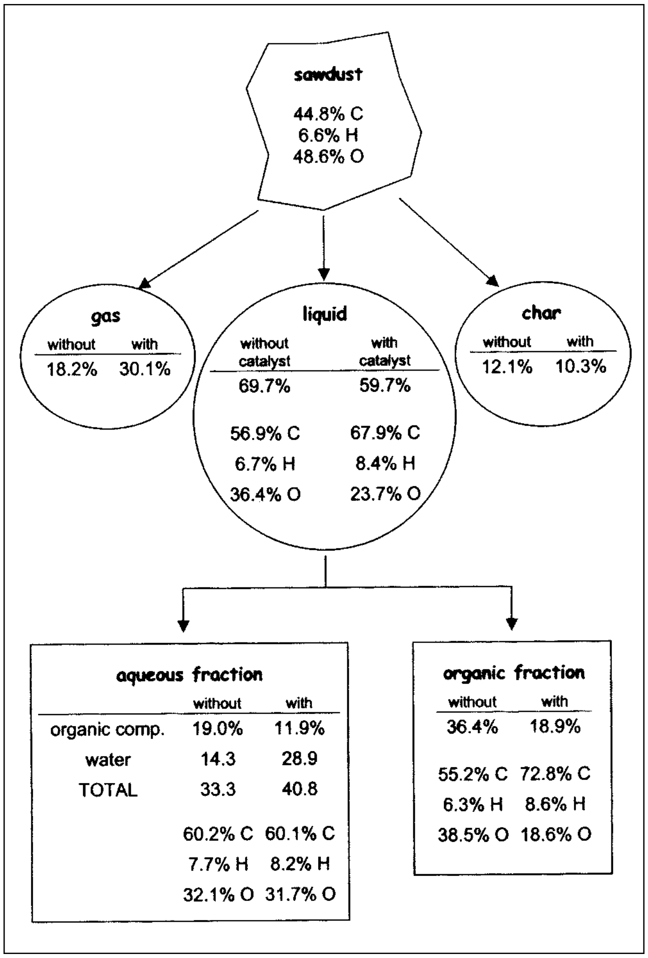

Figure 10. Effect of the catalyst on global yields and composition of pyrolysis products, at 450°C.

From this point of view, the "slightly evolved" nature of the liquid pyrolysis product, obtained by means of the technology proposed in this article has good prospects for obtaining high yields of aromatics by catalytic transformation, where there are no condensation compounds or polynuclear aromatics compounds.

Nevertheless, the conditions for catalytic transformation used in the literature are very different as far as catalyst, temperature, space–time, and reaction medium are concerned. Chantal et al. (1984) use He as inert gas, whereas Mathews et al. (1985) use H_2. Sharma and Bakhshi (1993b) obtain a maximum yield of aromatics of 19.9 wt % at 370°C, but with a 50 wt. % yield of coke and char.

The main function of the catalyst is the reduction of the oxygen content in the liquid-pyrolysis product, as is clearly seen in Figure 10, in which the product yields and the percentage of C, H and O of the liquid product obtained with and without the catalyst at 450°C are shown. As is observed, the composition of the aqueous-liquid fraction is modified by using the catalyst and considerable deoxygenation of this product, whose empirical formula (without taking the content of water into account) is $CH_{1.41}O_{0.48}$ without catalyst and $CH_{1.48}O_{0.26}$ with catalyst is attained. The organic fraction becomes less oxygenated by the action of the catalyst, so the empirical formula is $CH_{1.37}O_{0.52}$ without catalyst and $CH_{1.42}O_{0.19}$ with catalyst.

Conclusions

The conical spouted-bed reactor behaves well hydrodynamically for catalytic pyrolysis of biomass residues, which makes it a good alternative to the already accepted technology for pyrolysis in fluidized beds and the catalytic transformation of the liquid product in another reactor. The use of the catalyst *in situ* in the spouted-bed reactor is possible thanks to its reduced segregation and to the excellent gas−solid contact, which allows the isothermal regime in the bed to be attained at temperatures below 500°C, which is suitable for a good HZSM-5 zeolite performance in a reaction medium where there is steam.

The use of the catalyst is outweighed by an important modification in product distribution; that is, an important increase in gases, which results in a decrease in the yield of liquids, and, to a lesser extent, of char. A high degree of deoxygenation of the liquid product is attained by water formation, which is present in the aqueous fraction. Decarboxylation decreases with respect to that in pyrolysis without catalyst and, consequently, CO_2 yield decreases. At 450°C the yield of H_2O is 14.3 wt. % without catalyst and 28.8 wt. % with catalyst. These results show that the use of the HZSM-5 zeolite yields to a profound modification in the pyrolysis yield, and this modification is much greater than that obtained by modifying the operating variables in flash pyrolysis without catalyst.

On the other hand, the yield of aromatics in the liquid fraction and of hydrocarbons in the gases augur well for a catalytic transformation integrated into pyrolysis in a spouted bed. Nevertheless, the complexity of this process requires more detailed studies on the effect of space−time (amount of catalyst) and deactivation and regeneration of the catalyst. The objective of these studies will be the optimization of the operating conditions in order to obtain a liquid product with a more suitable composition for its use as fuel.

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