

Undesired components in the transformation of biomass pyrolysis oil into hydrocarbons on an HZSM-5 zeolite catalyst

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Abstract: The results of the catalytic transformation on HZSM-5 zeolite of mixtures of components of biomass pyrolysis oil in the 673–723 K temperature range are evidence of the need for previously separating certain components (aldehydes, oxyphenols and furfural) that undergo severe thermal degradation by forming carbonaceous deposits at the reactor inlet ducts and on the catalyst itself. The deactivation of the catalyst is a consequence of the deposition of two different types of coke: one of catalytic origin (similar to that generated in the transformation of methanol and bioethanol) and the other of thermal origin, which is produced by the aforementioned degradation. The remaining oxygenate components react to each other with synergistic effect, which means that their reactivity is higher than that of the pure components. The results show that the aqueous fraction of biomass pyrolysis oil may be transformed into hydrocarbons on acid catalysts similarly to the more familiar transformation of methanol and bioethanol.

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Keywords: biomass pyrolysis oil; bio-oil; HZSM-5 zeolite; oxygenates; coke deactivation

NOTATION

- C_c Coke content, referred to catalyst mass (% wt)
 F_o Mass flow rate of oxygenates in feed (g h^{-1})
 T Temperature (K)
 W Catalyst weight (g)
 X_i Concentration of component i (% wt by mass unit of organic components)
 $X_{w/o}$ Water/oxygenate mass ratio in feed

INTRODUCTION

Biomass has the potential to become one of the major global primary energy sources over the next century, and modernised bioenergy systems are proposed as important contributors to future sustainable energy systems and to sustainable development in industrialised countries as well as in developing countries. In particular, the valorisation of forest wood and of residues from agriculture and forestry is identified as a potential major source of biomass for energy in several studies (with a maximum potential of 1135 EJ year⁻¹ in 2050 (where 1 EJ = 10¹⁸ J = exajoule)).^{1,2}

The production of bio-oil by flash pyrolysis is one of the more encouraging routes for valorisation of biomass.^{3,4} Bio-oil has attracted much attention in recent years owing to its potential as a fuel for diesel

engines (in emulsion with fuel oil)^{5,6} or for catalytic transformation into products of energetic interest or suitable as raw materials in petrochemistry.^{7–11} Bio-oil has a very complex nature: more than 300 components have been determined qualitatively and more than 40 quantitatively.^{12,13} Generally, bio-oil is obtained at the outlet of the reactor and consists of two well-differentiated fractions, namely the oxygenates soluble in water and the fraction made up by pyrolytic lignin.^{12,14,15}

When acid catalysts are used (silica/aluminas and HZSM-5 and HY zeolites), the aqueous fraction of bio-oil undergoes efficient dehydration and cracking by formation of C₄–olefins and C₁₂–aromatics.^{8–11,16–18} Thus the catalytic transformation of bio-oil, given its oxygenate nature, performs similarly to MTO (methanol-to-olefins), MTG (methanol-to-gasoline) and BTG (bioethanol-to-gasoline) processes. Nevertheless, severe operational problems occur in the catalytic transformation of bio-oil, caused by the deposition of carbonaceous material inside the pipelines leading to the reactor inlet and on the catalyst.^{7,16–19} In view of this situation and given the complexity of bio-oil, it is convenient to ascertain the possibilities of catalytic transformation of the individual components and fractions of bio-oil. In previous

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papers the behaviour of alcohols, acids, aldehydes, ketones and phenols has been studied separately.^{20,21}

In this paper the transformation of mixtures of representative compounds of bio-oil has been studied, with the aim of determining possible synergistic effects between reactants and products, especially those that lead to the formation of carbonaceous deposits in the catalytic transformation of bio-oil. This information is interesting for modifying the conditions of the process in order to improve the composition of the bio-oil or to modify this composition by separating undesired components.

EXPERIMENTAL

Catalyst

An HZSM-5 zeolite catalyst has been used, prepared by agglomerating HZSM-5 zeolite (25 wt%) with bentonite (Exaloid, Arceniega, Spain; 30 wt%) using fused alumina (LaRoche, Baton Rouge, LA, USA) as inert charge (45 wt%). The HZSM-5 zeolite has been synthesised with an Si/Al ratio of 24, following Mobil patents.^{22,23} The calcination temperature of 570 °C for 2 h in an N₂ stream is suitable for obtaining an acid structure. The resulting catalyst has been proven to be hydrothermally stable for the MTG (methanol-to-gasoline) process carried out following reaction-regeneration cycles.²⁴

The physical properties of the catalyst, determined by N₂ adsorption-desorption in a Micromeritics (Norcross, GA, USA) ASAP 2000, are: surface area, 131 m² g⁻¹; pore volume, 0.43 cm³ g⁻¹; apparent density, 1.21 g cm⁻³; real density, 2.53 g cm⁻³. The contribution of pores of different sizes to the total pore volume is: $d_p < 10^{-3}$ µm (micropores), 8.1%; $10^{-3} < d_p < 10^{-2}$ µm (mesopores), 14.7%; $10^{-2} < d_p < 2$ µm (macropores), 77.2%.

Figure 1 shows the results of TPD (temperature-programmed desorption) of NH₃ for the fresh catalyst. These results have been obtained in an SDT 2960 thermobalance (TA Instruments, New Castle, DE, USA) connected online to a ThermoStar mass spectrometer (Balzers Instruments, Asslar, Germany). The catalyst's total acidity (up to 0.12 mmol NH₃ g⁻¹ catalyst) and distribution of acid strength (with most of the sites having an adsorption heat of 140 kJ mol⁻¹ NH₃) have also been determined by means of this equipment. The Brønsted/Lewis site ratio, determined by FTIR analysis (Nicolet 740 provided with a Spectra Tech (Waltham, MA, USA) chamber) of adsorbed pyridine, is 3.4. This ratio corresponds to the intensity ratio of bands at 1550 cm⁻¹ (Br-Py bonds) to those at 1450 cm⁻¹ (Lw-Py bonds).

Reaction and analysis equipment

The reaction equipment has been described in detail elsewhere and is operated by means of a data acquisition and control program.²⁵ The reactor is made of 316 stainless steel, with 9 mm internal diameter.

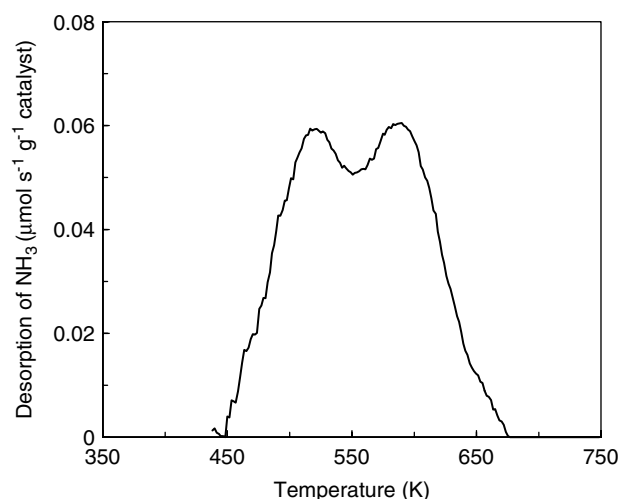


Figure 1. Desorption at programmed temperature of ammonia adsorbed at 423 K in catalyst.

It is provided with a fixed bed of catalyst diluted with alumina as inert and operates in the isothermal regime. Before the reactor entrance, in the preheating zone, there is a steel filter for retaining most of the carbonaceous residue formed by degradation of certain reactants. The reaction products are analysed by gas chromatography (Hewlett Packard 6890; Ramsey, MN, USA) by means of detectors based on thermal conductivity (TCD) and flame ionisation (FID).

Two mixtures made up of oxygenate components with the compositions shown in Table 1 have been prepared. These compositions have been established bearing in mind the composition of flash pyrolysis bio-oil¹² and with the aim of paying special attention to the simultaneous presence of acetaldehyde and phenol (mixture 1) and of 2-methoxyphenol and furfural (mixture 2).

Subsequent to each run the catalytic bed is subjected to stripping with He for 0.5 h at the reaction temperature, with the aim of eliminating the reaction medium components that may remain adsorbed on the catalyst. The total amount of catalyst contained in the bed is homogenised in order to take a sample for coke measurement. This measurement is carried out in a

Table 1. Composition (% wt) of mixtures of oxygenate components

Component	% in mixture
<i>Mixture 1</i>	
Acetone	47.0
Acetic acid	23.5
Methanol	6.0
2-Butanol	3.5
Phenol	14.0
Acetaldehyde	6.0
<i>Mixture 2</i>	
Acetone	46.0
Acetic acid	23.0
2-Methoxyphenol	13.0
2-Propanol	9.5
Furfural	8.5

simultaneous SDT 2960 thermobalance (TA Instruments) by combustion of the coke with air following a temperature ramp of 3 K min^{-1} from 573 to 823 K and maintaining this temperature constant for 1 h in order to ensure total elimination of the coke. Prior to the combustion step the samples of deactivated catalyst are subjected to a sweeping step in the thermobalance with He at 823 K for 0.5 h in order to attain the coke aging required for reproducing the results of combustion.²⁶

RESULTS

Composition of product stream

Figures 2 and 3 show the results of evolution with time on stream of the organic components of the outlet stream for the catalytic transformation of mixture 1, diluted at 50% wt with water, for a space time of $0.176\text{ g catalyst h g}^{-1}$ oxygenates. Figure 2 corresponds to 673 K and Fig 3 to 723 K.

Figure 2 shows that, when the catalyst is not deactivated, the main reaction products are *i*-butene and C_{5+} olefins, followed by propene and *n*-butenes, and the conversion to aromatics and C_{4+} paraffins is

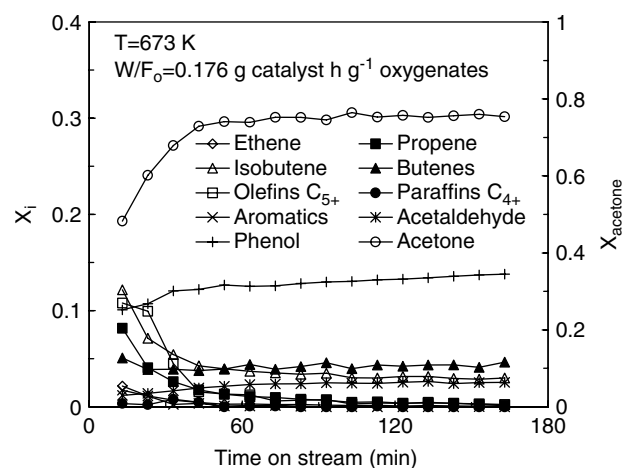


Figure 2. Evolution with time on stream of reaction products in catalytic transformation of mixture 1 at 673 K.

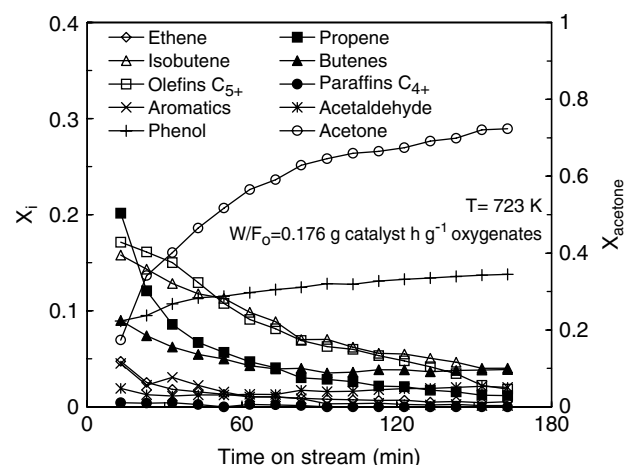


Figure 3. Evolution with time on stream of reaction products in catalytic transformation of mixture 1 at 723 K.

very low. The deactivation of the catalyst is very rapid and, consequently, the concentration of the reaction products at the outlet of the reactor decreases very fast. There are two exceptions, the first being the formation of *n*-butenes, whose composition is almost constant with time on stream, and the second being that of *i*-butene, whose concentration decreases monotonically to a steady value. The high final concentration of butenes at the outlet stream is due to the fact that butenes are the primary products in the dehydration of 2-butanol, whose conversion is complete.²⁰

Figure 2 also shows that the concentration of acetaldehyde at the outlet stream is very low (around half of that in the feed) and hardly changes throughout the reaction time. This result is not due to the catalytic transformation of this compound, whose low reactivity has been proven in a previous paper,²¹ but to its degradation to 'thermal coke' in a proportion near 50% wt.

Furthermore, acetic acid is totally converted, transforming mainly into acetone, which confirms the high percentage of acetone in the product stream, although it is partially converted into hydrocarbons. The transformation of acetic acid into acetone on HZSM-5 zeolite takes place mainly by decarboxylation, but dehydration is less favoured and decarbonylation even less so.^{21,27}

The level of conversion of acetone at 673 K agrees with that corresponding to this oxygenate when it is fed diluted with water at 50% by volume.²¹

Figure 4 shows the scheme of reaction for the transformation of acetone.²¹ Acetone dehydrates to *i*-butene and, subsequently, *i*-butene evolves to C_{5+} olefins at temperatures above 350°C . These in turn produce C_{5+} paraffins and aromatics, the proportion of aromatics being much higher than that obtained from alcohols. Ethene, propene and butenes are obtained at high temperature from cracking reactions. Nevertheless, acetone is less reactive than alcohols and, consequently, higher space times are required for obtaining high conversion. The values of composition of aromatics (mainly made up of toluene, followed by xylenes and, to a lesser extent, benzene) shown in Fig 2 are a consequence of the lower space times used in this paper (five times lower) than others previously used for the transformation of acetone.^{21,27}

Furthermore, it is observed that the conversion of acetic acid into acetone is higher than that determined in the transformation of acetic acid diluted with 50% water by volume under similar conditions

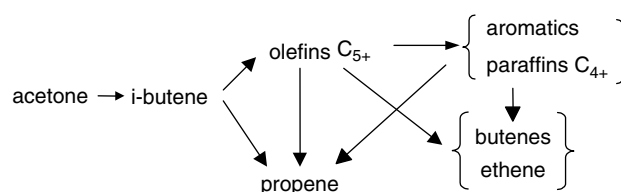


Figure 4. Reaction scheme for transformation of acetone on HZSM-5 zeolite.²¹

of temperature and space time.²¹ This synergistic effect is in agreement with that observed in the transformation of acetic acid and is explained by the autocatalytic effect of the initially formed acetone in the transformation of acetic acid. In this case, when a high proportion of acetone is fed together with acetic acid, the result is the total conversion of the acid in the whole range of time on stream studied. Subsequently, acetone is transformed into hydrocarbons as has been previously explained when acetone is fed.

Figure 2 also shows that phenol conversion is low, which agrees with the previous results obtained for the transformation of phenol diluted with water.²⁰ This result shows the low reactivity of phenol with the other components of the mixture and with their products. The reduced transformation of phenol reinforces interest in the strategy of separating of phenols from the pyrolysis liquid product prior to its valorisation by catalytic transformation.

Figure 3, corresponding to 723 K, shows that the initial conversion of acetone is considerably higher than that previously observed at 673 K and that the concentrations of propene and ethene increase considerably, which is a consequence of the importance of cracking at this temperature. Significant quantities of aromatics and, to a lesser degree, C₄₊ paraffins are also observed. The deactivation of the catalyst is also very rapid, which mainly affects the final reaction products (aromatics, C₄₊ paraffins, ethene and propene) and, to a lesser degree, the intermediate products in the reaction kinetic scheme (i-butene, n-butenes and C₅₊ olefins). In this case the conversion of 2-butanol to butenes is also complete, even when the catalyst is almost totally deactivated for the formation of the remaining hydrocarbons, and the conversion of acetic acid to acetone is also upheld when the catalyst is severely deactivated.

For the reaction at 673 K the total content of residue deposited at the reactor inlet is 4.9% wt of the total organic feed into the reactor, and for the reaction at 723 K this residue is 5.8% wt of the organic feed.

The first runs with mixture 2 of Table 1 have been carried out by feeding 50% wt of water, as was done previously with most of the pure feeds^{20,21} and with mixture 1. The results obtained for the reaction products do not agree with the reactivity of the pure components. Thus the amount of non-reactive components such as methoxyphenol is insignificant at the reactor outlet stream. Moreover, the fact that the catalytic bed is blocked by carbonaceous material is evidence that a component of the reaction mixture is converted to this undesired product. These results and the previous information in the relevant literature concerning the formation of a large amount of carbonaceous material^{8–10,17,18} attribute the formation of these components either to the thermal degradation of furfural, as was previously observed for acetaldehyde,²¹ or to the expected degradation of methoxyphenol,²⁰ although it may be due to the formation of polymers by reaction

of methoxyphenol and furfural. This degradation explains the almost total absence of these components in the product stream.

Figure 5 shows the results corresponding to the evolution of the products with time on stream for a reaction at 673 K with a space time of 0.053 g catalyst h g⁻¹ oxygenates and 90% wt of water in the feed for mixture 2. In spite of the high concentration of water (which may attenuate the polymerisation of these components and their degradation to carbonaceous material), there is no 2-methoxyphenol or furfural in the product stream. The main reaction product is propene, which in this case is the primary product of 2-propanol dehydration, and the formation of butenes (which are primary products in the transformation of acetone) is also important and, to a lesser degree, that of C₅₊ olefins and aromatics.

The presence of 2-propanol in the product stream is also noteworthy, in a concentration of 13.4% wt (by mass unit of organic components). This is evidence that 2-propanol dehydrates to propene (whose concentration is high), but although this dehydration requires few acid sites, it is affected by deactivation owing to the low space time used. The reactivity of the acetic acid in the mixture to give acetone is also proven, although deactivation is significant owing to the low space time used.

The result obtained for the reactivity of mixture 2 following a temperature–time sequence is noteworthy. This is shown in Figs 6 and 7, corresponding to two values of space time. The run corresponding to Fig 6 has been carried out with the same values of space time and water content in the feed as in the run of Fig 5, whereas Fig 7 corresponds to a double value of space time.

In Fig 6 it is observed that, above 573 K, 2-methoxyphenol and furfural, which are responsible in this case for the formation of the carbonaceous residue, are not present in the product stream. The deposition of carbonaceous residue with this feed is higher than with mixture 1 (given the higher proportion of

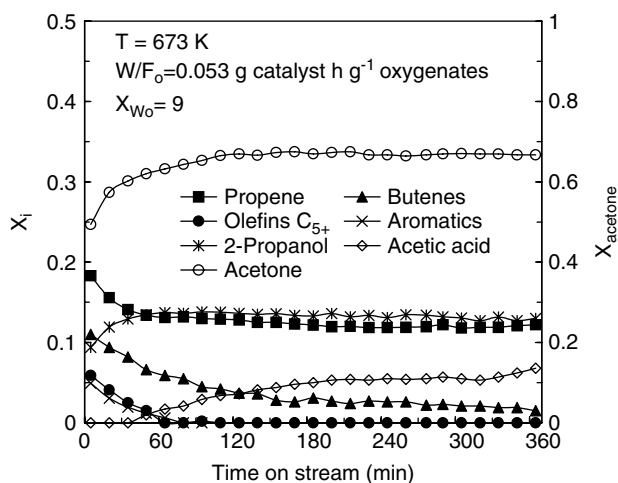


Figure 5. Evolution with time on stream of reaction products in catalytic transformation of mixture 2 at 673 K

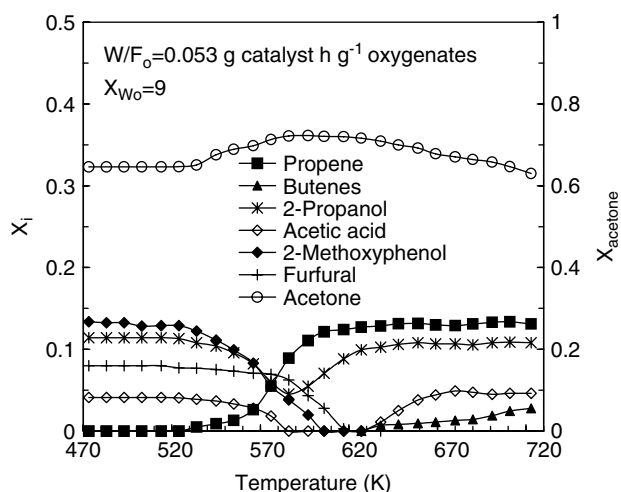


Figure 6. Effect of reaction temperature on distribution of products in catalytic transformation of mixture 2 for $W/F_o = 0.053 \text{ g catalyst h g}^{-1}$ oxygenates

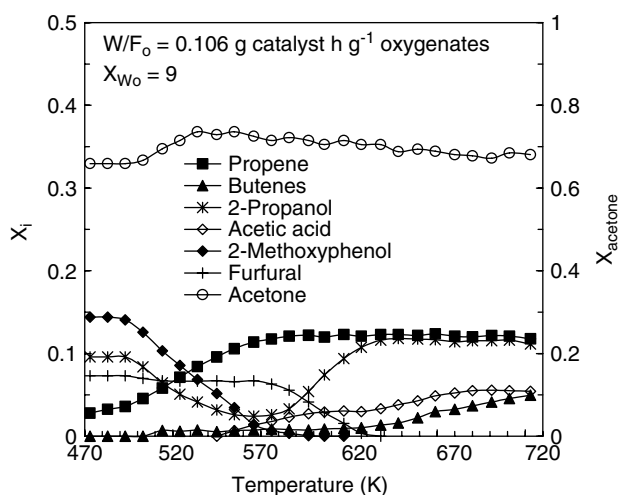


Figure 7. Effect of reaction temperature on distribution of products in catalytic transformation of mixture 2 for $W/F_o = 0.106 \text{ g catalyst h g}^{-1}$ oxygenates

the components responsible for the deposition), which contributes, to a large extent, to the deactivation of the catalyst and, consequently, the rate of transformation of the other components of the mixture is reduced. This explains why even 2-propanol is present in the product stream in a significant concentration. As a consequence of the severe deactivation of the catalyst, the only reaction products are the primary products in the dehydration of propanol (propene) and acetone (butenes, mainly *i*-butene), but no hydrocarbons of more than four carbon atoms are obtained.

The results of Fig 7 correspond to a space time that is twice that of Fig 6 and are evidence that a greater amount of catalyst does not solve the problem (although it may play the role of a 'filter' for the retention of the 'thermal coke'), because no hydrocarbons of more than four carbon atoms are obtained. This result means that it is impossible to directly treat mixtures with these components (2-methoxyphenol and furfural).

Coke deposition and its nature

Table 2 shows the values of total coke content deposited on the bed for the catalyst samples deactivated in the transformation of the two mixtures of oxygenates under different operating conditions. The results correspond to cokes aged subsequent to the sweeping with helium at 823 K for 30 min. In all samples the coke deposited externally on the catalyst particle was previously eliminated by a physical process (sieving).

As was observed for the feeds made up of individual oxygenate components,^{20,21} in Table 2 it is observed that an increase in reaction temperature leads to a considerable increase in coke content. Furthermore, the lower amount of coke obtained for the feeds of mixture 2 is mainly due to the fact that the water content of this mixture is much higher than that of mixture 1, and water contributes greatly to attenuating coke deposition, as has already been proven in other processes of catalytic transformation of oxygenates.^{25,28}

Figure 8 shows the evolution of the DTG curve (expressed as mass change by time unit and catalyst mass unit) for the combustion of the aged coke deposited on the catalyst in the run of transformation of synthetic mixture 1 at 673 and 723 K. It is observed that, as in the case of the feed made up of pure acetaldehyde and 2-methoxyphenol,²⁹ there are two different fractions of coke. The first fraction, which burns at lower temperature, is the 'thermal coke', which is probably the residue deposited on the matrix of the catalyst particles and which is related to the residue deposited on the device placed at the reactor inlet during feed preheating. The second fraction corresponds to the internal 'catalytic coke' located in the HZSM-5 zeolite, which burns at higher temperature, given its less hydrogenated nature. The level of hydrogenation of the coke and the H/C ratio have been determined in studies such as those shown in Figure 9, where the amount of coke eliminated as water, CO and CO₂ during combustion of the catalyst sample deactivated in the run at 673 K has been plotted as an example.

For the reaction at 673 K the first fraction burnt is 63% wt of the total coke eliminated in the combustion. In the reaction at 723 K the fraction of the coke that burns at higher temperature (catalytic coke) is significantly greater, corresponding to the increase in

Table 2. Coke content in catalyst deactivated under different reaction conditions

Mixture	X_{W_o}	$T \text{ (K)}$	W/F_o (g catalyst h g ⁻¹ oxygenate)	Time on stream (h)	C_c (% wt)
1	1.26	673	0.176	3	7.95
		723	0.176	3	8.41
2	9	673–723	0.053	4.2	3.04
			0.106	4.2	3.07
		673	0.053	6	6.07

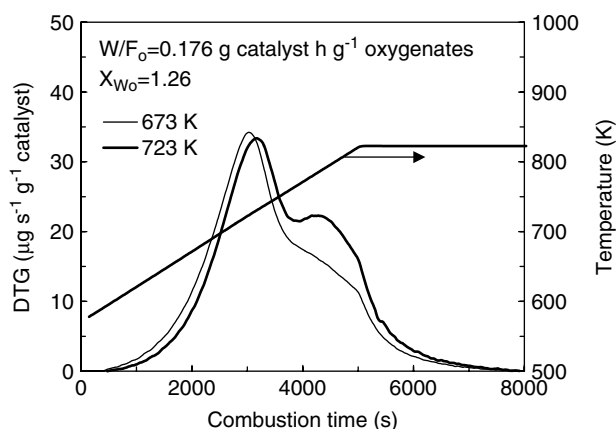


Figure 8. Evolution with time on stream of mass change (DTG) during combustion of coke deposited in catalytic transformation of mixture 1 at 673 and 723 K

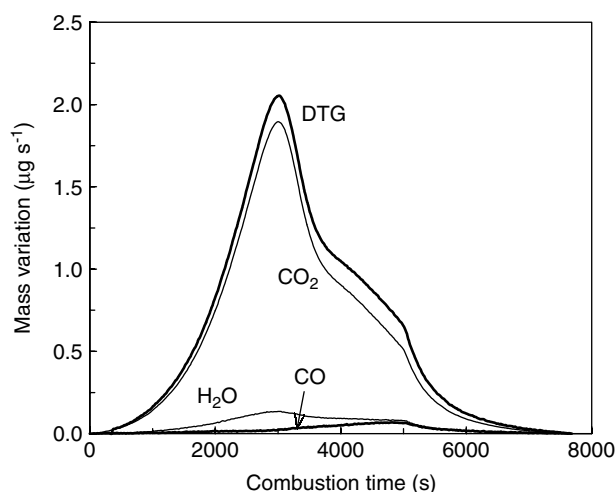


Figure 9. Evolution with time on stream of combustion products of coke deposited in catalytic transformation of mixture 1 at 673 K

coke content with temperature, as has been proven for the feeds made up of model components.^{20,21} Nevertheless, the proportion of the first coke fraction (thermal coke) is almost equal to that corresponding to the run at 673 K, although it is appreciated that the position of the maximum is slightly displaced at a higher temperature, which is evidence that it is a slightly more evolved coke (with a lower H/C ratio).

Figures 10 and 11 show the DTG curves corresponding to the combustion of coke deposited for mixture 2. Figure 10 corresponds to the coke of the catalyst deactivated at 673 K (Fig 5), which was burnt following a heating ramp of 5 K min⁻¹ from 573 to 873 K. Figure 11 corresponds to the combustion of the coke of the catalyst deactivated in the dynamic runs following a temperature ramp (Figs 6 and 7).

The aforementioned two fractions of the coke are also observed in Figures 10 and 11. In Fig 11 it is observed that the second fraction or 'catalytic coke' is almost negligible compared with the 'thermal coke', which is explained because the catalyst is severely deactivated and the conversion to products is very low, as has been observed in the kinetic study

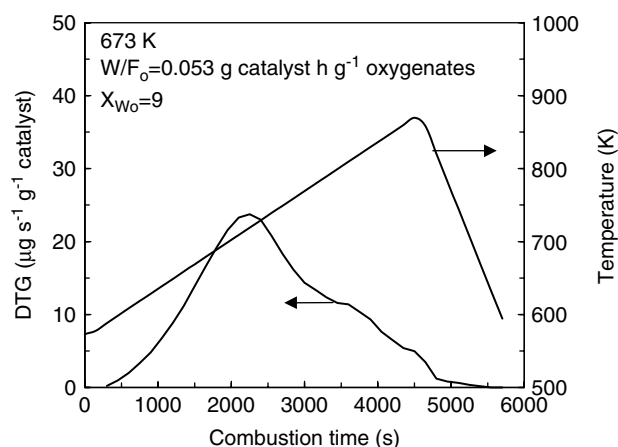


Figure 10. Evolution with time on stream of mass change (DTG) during combustion of coke deposited in catalytic transformation of mixture 2 at 673 K

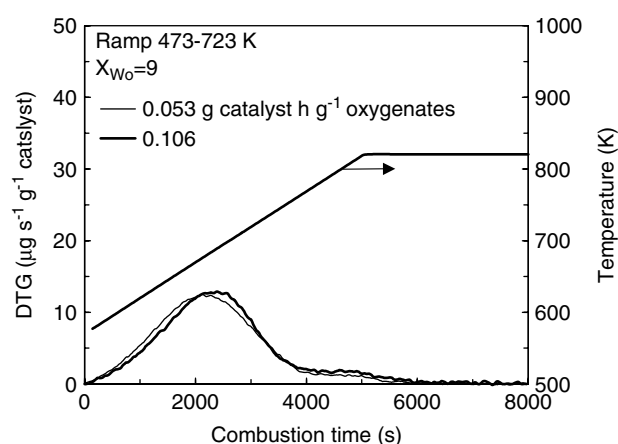


Figure 11. Evolution with time on stream of mass change (DTG) during combustion of coke deposited in catalytic transformation of mixture 2 for runs with temperature ramp from 473 to 723 K

corresponding to these runs. This rapid deactivation is a consequence of the importance of the deposition of the thermal coke from low temperatures.

The DTG curve of Figure 10, corresponding to the reaction temperature of 673 K, is similar to that obtained for mixture 1 at the same temperature (Fig 8). As is observed in this curve, the proportion of 'catalytic coke' is much higher than that in Fig 11. Moreover, the first peak in the DTG curve for the combustion of the 'thermal coke' appears at a slightly lower temperature (around 45 K lower) than that corresponding to the 'thermal coke' deposited in the case of synthetic mixture 1. This difference between the peaks corresponding to 'thermal coke' is the same as that observed for the 'thermal cokes' deposited with the feeds of acetaldehyde and 2-methoxyphenol.²⁹

CONCLUSIONS

The reactivity observed for a feed made up of a mixture of acetone, acetic acid, acetaldehyde, phenol, 2-butanol and methanol agrees with the results obtained for the feeds of pure components on a catalyst of

HZSM-5 zeolite. Thus, initially, a high proportion of C₅₊ olefins, butenes and propene and, to a lesser degree, aromatics and paraffins C₄₊ is obtained. Furthermore, a synergistic effect is observed owing to the high reactivity of some of the primary products.

The catalyst undergoes severe deactivation and, consequently, the concentration of all the reaction products except butenes (which are formed by butanol dehydration and are the first step in the transformation of acetone) decreases very rapidly. The coke of thermal origin, generated by degradation of acetaldehyde, contributes to deactivation.

The mixture of oxygenates containing 2-methoxyphenol and furfural is of very low reactivity owing to the fact that the reaction between these components, even at a very low temperature, produces a carbonaceous residue that deactivates the catalyst. The degradation to coke that 2-methoxyphenol undergoes in the presence of furfural is higher than that corresponding to pure 2-methoxyphenol.

Consequently, the feasibility of the process of transformation of bio-oil into hydrocarbons on acid catalysts requires the previous separation of certain components of the bio-oil, such as aldehydes, oxyphenols, furfural and their derivatives.

The coke deposited on the catalyst consists of two well-differentiated fractions: one that burns at a higher temperature (catalytic coke) and another more hydrogenated that burns at a lower temperature, which is related to the pyrolytic char or carbonaceous residue that is deposited even at the reactor inlet by condensation–degradation of the aforementioned components.

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