REACTIONS OF BIOMASS PYROLYSIS OILS OVER ZSM-5 ZEOLITE CATALYSTS

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INTRODUCTION

It has been shown that synthetic zeolites such as ZSM-5 can be used to convert oxygenated compounds derived from biomass materials into hydrocarbon compounds which can be used as fuels and chemical feedstocks (1,2,3,4).

However, the pyrolysis oils obtained from woods by different thermoliquefaction processes (5,6), show poor hydrocarbon yield and high tar content when contacted over ZSM-5 zeolite catalysts at high temperature (7,8). Since the pyrolysis oils are composed of a wide variety of oxygenated compounds such as cyclopentanone, furfural, phenol, acid and carbohydrate derivatives (9,10), it is difficult to point out exactly which family of compounds is contributing more to the observed tar content and to the deactivation of the catalysts. Catalytic studies on model compounds which are generally found in the pyrolysis oils are therefore primordial in order to determine the best catalytic system. The reactions of phenolic compounds over ZSM-5 catalysts are already reported (8). The present paper thus reports the results for the conversion of cyclopentanone, furfural, glucose and its isopropylidene derivative over H-ZSM-5, Zn-ZSM-5 and Mn-ZSM-5 zeolite catalysts at temperatures ranging from 400°C to 500°C. Some reactions are supplemented with methanol in their feeds so as to determine the effect of increased hydrogen to carbon effective ratio on the deoxygenated hydrocarbon yields.

EXPERIMENTAL

Preparation and caracterization of catalysts

The ammonium form of ZSM-5 was prepared according to a published procedure (11). The H-form of the catalyst was obtained by calcination at 500°C for 10 hours. The zinc and manganese loaded catalysts were prepared by ion exchange in a 10% aqueous solution of $Zn(NO_3)_2$ and $Mn(NO_3)_2$ at ~ 80°C. After washing and drying at 160°C over night, the solid was calcined for 10 hours at 520°C. The X-ray diffraction pattern of the three synthetic ZSM-5 are similar to those reported in the litterature. The chemical composition of ZSM-5 samples are shown in table 1.

Apparatus

The catalytic conversion were studied in a continuous flow quartz reactor with a fixed bed of diluted catalysts. The reaction conditions are reported in table 1. After an experimental run (about 3 hours), the tar on the catalytic bed was determined by taking the difference in weight of the reactor before and after placing it in a furnace set at 500°C on the presence of air. The reaction products were analyzed by GC and GC/MS (table 1).

RESULTS AND DISCUSSION

Figure 1 shows the yield of conversion, C_1 - C_6 aliphatics, aromatics, polyaromatics and tar as a function of reactor temperature for pure cyclopentanone over H-ZSM-5/bentonite (80/20) catalyst. The conversion is completed at 350°C. The

main reaction is thermal decarbonylation giving C_4 hydrocarbons that react further on the catalytic bed to produce aliphatic aromatic and polyaromatic hydrocarbons.

Table 2 shows the reaction of pure furfural (H/C_{eff}= 0) over various cation exchanged ZSM-5 catalysts at 400°C. The deoxygenated hydrocarbon yields range from 6.6 to 9.4% and the oxygenated hydrocarbon yields range from 25.6 to 50.0%. These values reflect the poor performance of all three catalysts in deoxygenating furfural. The large quantities of furan and CO observed is due to thermal decarboxylation of furfural. Higher tar contents were observed for the metal exchanged catalysts (21.2 and 25.9%) than the hydrogen exchanged catalyst (14.2%). The low water contents (range of 2.7 to 7.0) produced from these reactions indicate poor catalytic deoxygenation of furfural. CO_2, which is produced from pyrolytic reactions, is obtained in low yields. The yields for the aliphatics (9.0 ± 1.4%) and olefins (8.5 ± 2.1%) are comparatively smaller than those for the aromatics (47.7 ± 3.5%) and polyaromatics (34.7 ± 3.8%). Polyaromatics are usually produced on the surface of the zeolite because they are too large to enter or leave the channels of the zeolite; high values for these compounds are indesirable because they are not usefull as chemical feedstocks.

Figure 2 shows the product distributions for the reaction of various furfural/methanol mixtures over H-ZSM-5/bentonite (80/20) at a reactor temperature of 450°C; only the major components in the products are shown. The abscissa in figure 2 is given in both increasing percentage of methanol and increasing $(H/C)_{eff}$for the feed. As methanol increases the yields for deoxygenated hydrocarbons and water increase while those for tar, furan and CO decrease. The drastic increase of deoxygenated compounds and water and decrease of furan with increasing methanol concentration indicate that significant catalytic deoxygenation is taking place. At about 55% methanol/45% furfural $(H/C)_{eff}$ of 0.85, there is complete removal of furan from the reaction products; only small quantities of other oxygenated hydrocarbons were present (< 0.26%). The yields for the other products were similar to those observed previously for furfural. Only at 70% methanol/30% furfural there was a significant reduction in the tar content, i.e. 6.7% (14.1% on carbon basis). The average CO_2 present was 0.3 ± 0.1%.

Table 3 shows the product distribution for reactions of furfural/methanol (30/70) over various concentrations of H-ZSM-5 at 450°C. By diluting the catalyst with bentonite from 80 to 18%, the deoxygenated hydrocarbon yield increased from 30.6 to 41.4%. Changing the support material from bentonite to Al_2O_3/SiO_2 caused a small reduction in the deoxygenated hydrocarbon yield (36.3%); there was, however, less coke formed when compared to the other two cases. The product selectivities were similar to those of previous cases.

Table 4 shows results for reactions of glucose and glucose derivative done over 80% H-ZSM-5 and 20% bentonite at 450°C. With an increased $(H/C)_{eff}$, there were increased deoxygenated hydrocarbon yields for the glucose/methanol/water (20.0/30.0/50.0) and glucose derivative/methanol/water (27.6/60.2/12.2) cases when compared to that of the glucose/water (20.3/79.7) case. Also, there was a simultaneous decrease in tar content with an increase in $(H/C)_{eff}$. However, in all cases the hydrocarbon yields are poor and the tar contents are too high. The high water content observed in all experiments (29.2 to 66.1%) is not only due to catalytic deoxygenation through loss of water but also due to polycondensation reactions of glucose and its derivative. These condensation reactions produce polymeric oxygenated compounds which are responsible for the high tar content observed. Oxygenated hydrocarbons, CO and CO_2, are minor products which are normally obtained from thermal decomposition of biomass materials (12). The product selectivity indicates a high percentage of aliphatics (23.6 to 50.5%) and aromatics (34.2 to 53.2%).

Except for the reaction with glucose/water, the olefin contents are low for the other two reactions. The production of polyaromatics (mainly indene and naphthalene derivatives) is rather high (2.56 and 7.24%) considering that they are produced from the surface of the zeolite rather than in the channels of the zeolite.

To test the efficiency of the catalyst, experiments were done with 18% H-ZSM-5 (instead of 80%) dispersed in 82% bentonite. Also, the catalytic bed would have less acidic sites (Brönsted sites) which are known to promote polymerization of the carbohydrates and hence reduce the deoxygenated hydrocarbon yield. Table 5 shows the results for experiments done on the diluted catalytic bed. Only in the glucose/methanol/water (20.0/30.0/50.0) case there was a significant increase in the deoxygenated hydrocarbon yield and a decrease in tar content. Hence, reducing the number acidic sites does not reduce the extent of the polymerization of the carbohydrates. However, there was an increase in the polyaromatic content in table 5 compared to that in table 4 indicating that there is more surface reaction in the dilute catalyst case.

When the catalytic support material was changed from bentonite to a mixture of Al_2O_3 and SiO_2, the yield of deoxygenated hydrocarbon increased for both cases as showed in table 6 when compared for similar cases in tables 4 and 5. There were also a comparable decrease in tar content for these reactions.

Deoxygenation of glucose/water (20.3/79.7) with manganese and zinc exchanged ZSM-5 are reported in table 7. There are a reduction in the deoxygenated hydrocarbon yields when compared to similar reactions in tables 4 and 5. The tar contents were just as high as the reactions before. The product selectivity which is normally influenced by these metal exchanged zeolites were not very different from those reported before.

CONCLUSION

Cyclopentanone is deoxygenated with high yield to hydrocarbons over H-ZSM-5 at 400°C. The reaction of furfural over ZSM-5 catalysts at 400°C and higher temperatures produce pyrolytic products which are volatile and non-volatile. The volatile fraction are deoxygenated to produce hydrocarbon products while the non-volatile fraction remain on the catalytic bed causing desactivation of the zeolite and enhancement of the tar content. Glucose and its isopropylidene derivative undergo thermal reactions which produce a significant amount of tar and a small amount of volatile products. The volatile fraction are deoxygenated by ZSM-5 catalysts to produce hydrocarbon products.

ACKNOWLEDGEMENT

This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada and from the Quebec Ministry of Science and Technology (Transfert of Technology University-Industry).

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TABLE 1

Chemical composition of ZSM-5 samples

Component (WT%)	H-ZSM-5	Mn-ZSM-5	Zn-ZSM-5
Na_2O	0.55	0.69	0.49
Al_2O_3	2.25	2.33	2.10
SiO_2	86.86	91.05	87.62
MnO	---	0.78	---
ZnO	---	---	0.26
TiO_2	0.59	0.64	0.38
L.O.I.*	7.62	3.26	6.68
Molar Ratio			
SiO_2/Al_2O_3	65.47	66.32	70.80
Na_2O/Al_2O_3	0.40	0.49	0.38

* L.O.I. means loss on ignition of sample weight.

REACTION CONDITIONS

Catalyst weight	:	10 g (80% ZSM-5 + 20% bentonite)
Temperature	:	350-560°C
Pressure	:	atmospheric pressure
Inert gas	:	helium (~ 3 mℓ/min)
WHSV **	:	variable
Reaction time	:	3 hours

** The weight hourly space velocity (WHSV) is defined as:

$$WHSV = \frac{\text{g of injected feed per hour}}{\text{g of catalyst}}$$

ANALYTICAL CONDITIONS

- Gas chromatography : HP 5890 GC with DB-5 (SE-54) column (30 m x 0.25 mm, 1.0 μ)
  - For liquid : 70°C (4 min), then 4°C/min to 160°C then 20 min at 160°C
  - Gas : 33°C (isothermal)
- GC/MS : HP 5890 GC and MS detector Pona column and DB-5 column

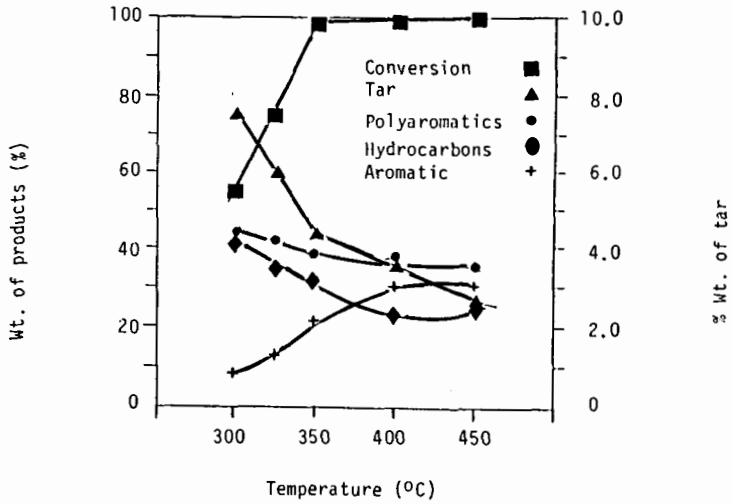

Figure 1: Reaction of cyclopentanone over H-ZSM-5/bentonite (80/20) at different reactor temperature

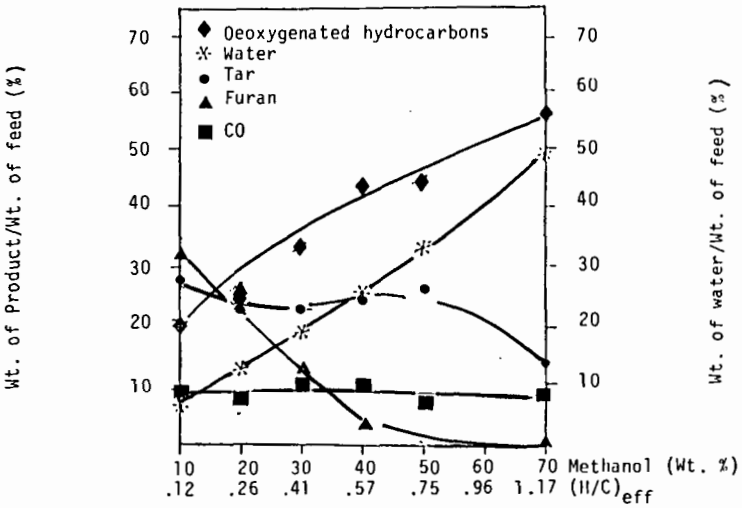

Figure 2: Reaction of furfural/methanol mixtures over H-ZSM-5/bentonite (80/20) at a reactor temperature of 400°C and a WHSV of .238 ± .018 hr^{-1}.

TABLE 2

Reaction of furfural over cation exchanges ZSM-5 at 400°C and WHSV of 0.281 hr^{-1}

Experimental conditions:

Catalyst composition:	80% H-ZSM-5 20% bentonite	80% Zn-ZSM-5 20% bentonite	80% Mn-ZSM-5 20% bentonite
Total product distribution (WT%)			
Furan	47.0	23.8	27.8
$\sum$ Oxygenated hydrocarbons	50.0	25.6	40.7
Tar	14.2	21.2	25.9
CO	22.8	36.3	17.9
CO_2	0.56	4.84	1.89
H_2O	4.39	2.69	6.97
Deoxygenated hydrocarbons	8.00	9.42	6.64
Product selectivity (WT%)			
Aliphatics, C_1 - C_8	8.84	7.62	10.5
Olefins, C_2 - C_6	8.46	10.6	6.48
Aromatics	50.6	48.8	43.9
Polyaromatics	32.1	32.9	39.1

TABLE 3

Reaction of furfural/methanol (30/70)feed ($(H/C)_{eff}$ of 1.17) over H-ZSM-5 at 450°C

Experimental conditions:

Catalyst composition:	80% H-ZSM-5 20% bentonite	18% H-ZSM-5 82% bentonite	18% H-ZSM-5 48% Al_2O_3 34% SiO_2
WHSV (Hr^{-1})	0.029	1.26	1.26
Total product distribution (WT%)			
Oxygenated hydrocarbons*	---	1.36	0.83
Tar	6.74	7.60	4.90
CO	9.44	7.84	7.25
CO_2	0.48	0.58	0.30
H_2O	52.7	41.6	50.4
Deoxygenated hydrocarbons	30.6	41.1	36.3
Product selectivity (WT%)			
Aliphatics, C_1 - C_8	1.82	11.6	20.7
Olefins, C_2 - C_6	2.90	3.01	3.63
Aromatics	83.5	72.8	60.8
Polyaromatics	11.9	12.6	14.8

* Mainly furan and benzofuran, derivatives and dimethylether.

TABLE 4

Reaction of glucose and glucose derivative over 80% H-ZSM-5 and 20% bentonite at 450°C

Experimental conditions:

Reactant composition:	20.3 glucose 79.7% water	20.0 glucose 30.0% methanol 50.0% water	27.6 glucose derivative 60.2% methanol 12.2% water
WHSV (Hr^{-1})	0.062	0.195	0.313
$(H/C)_{eff}$	0.0	1.59	1.36
Total product distribution (WT%)			
Oxygenated hydrocarbons	---	0.70*	3.87**
Tar	65.1	33.3	14.1
CO	2.14	0.46	0.23
CO_2	1.48	1.41	0.92
H_2O	29.1	59.7	66.1
Deoxygenated hydrocarbons	2.18	4.43	14.8
Product selectivity (WT%)			
Aliphatics, C_1 - C_8	23.6	35.7	50.5
Olefins, C_2 - C_6	41.6	3.81	2.74
Aromatics	34.8	53.3	43.2
Polyaromatics***	---	7.24	3.56

TABLE 5

Reaction of glucose and glucose derivative over 18% H-ZSM-5 and 82% bentonite at 450°C

Experimental conditions:

Reactant composition:	20.3% glucose 79.7% water	20.0% glucose 30.0% methanol 50.0% water	27.6% glucose derivative 60.2% methanol 12.2% water
WHSV (Hr^{-1})	0.862	1.195	1.12
$(H/C)_{eff}$	0.0	1.59	1.46
Total product distribution (WT%)			
Oxygenated hydrocarbons	0.58*	0.96*	4.20**
Tar	51.3	21.0	11.1
CO	3.79	1.76	0.84
CO_2	2.82	0.29	0.79
H_2O	39.4	57.9	64.3
Deoxygenated hydrocarbons	2.15	18.1	18.8
Product selectivity (WT%)			
Aliphatics, C_1 - C_8	29.0	43.6	17.5
Olefins, C_2 - C_6	7.33	1.18	14.0
Aromatics	45.2	45.3	55.8
Polyaromatics***	18.3	9.99	12.7

* Mainly furan and benzofuran derivatives; ** Mainly acetone and furan derivatives; ***Mainly indene and naphthalene derivatives

TABLE 6

Reaction of glucose and glucose derivative over 18% H-ZSM-5 and 48% Al_2O_3 and 34% SiO_2

Experimental conditions:

Reactant composition:	20.0 glucose 30.0% methanol 50.0% water	27.6 glucose derivative 60.2% methanol 12.2% water
WHSV (Hr^{-1})	1.18	1.11
$(H/C)_{eff}$	1.59	1.46
Total product distribution (WT%)		
Oxygenated hydrocarbons	0.12	0.24
Tar	14.3	6.86
CO	1.59	1.76
CO_2	0.44	0.47
H_2O	62.4	53.5
Deoxygenated hydrocarbons	21.2	37.2
Product selectivity (WT%)		
Aliphatics, C_1 - C_8	19.0	21.0
Olefins, C_2 - C_6	12.0	8.32
Aromatics	65.6	62.0
Polyaromatics	3.42	8.66

TABLE 7

Reaction of 20.3% glucose and 79.7% water over manganese and zinc exchanged ZSM-5

Experimental conditions:

Catalysis composition	80% Mn-ZSM-5 20% bentonite	80% Zn-ZSM-5 20% bentonite
WHSV (Hr^{-1})	0.046	0.055
$(H/C)_{eff}$	0.0	0.0
Total product distribution (WT%)		
Oxygenated hydrocarbons	---	---
Tar	72.3	53.1
CO	2.60	2.23
CO_2	1.91	4.19
H_2O	22.3	39.8
Deoxygenated hydrocarbons	0.89	0.68
Product selectivity (WT%)		
Aliphatics, C_1 - C_8	26.0	35.4
Olefins, C_2 - C_6	42.8	2.60
Aromatics	31.0	62.0
Polyaromatics	---	---