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Effect of H₂ as pyrolytic agent on the product distribution during catalytic fast pyrolysis of biomass using zeolites

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ABSTRACT

Bio-oil generated from catalytic fast pyrolysis or hydrotreating processes represents one of the most promising alternatives to liquid fossil fuels. The use of H₂ as carrier gas in the pyrolysis of biomass requires further research to study the catalytic fast pyrolysis reactions in case of using reactive atmosphere. In this work, pyrolysis experiments with lignocellulosic biomass have been performed in a fixed bed reactor in H₂ and N₂ atmospheres with/without HZSM-5 additions to investigate the influence of the pyrolytic agents during fast pyrolysis of biomass and upgrading of pyrolytic vapors over a zeolitic catalyst. It was found that in a H₂ atmosphere, H₂ was consumed in both non-catalytic and catalytic pyrolysis processes, respectively. Higher yields of non-aqueous liquids and permanent gases are obtained in a H₂ atmosphere compared to a N₂ atmosphere. A catalytic pyrolysis process using HZSM-5 in a H₂ atmosphere increased the production of PAHs (polymer aromatic hydrocarbons) and suppressed the production of MAHs (monomer aromatic hydrocarbons) compared to similar tests performed in a N₂ atmosphere. The results show an overall increased activity of HZSM-5 in the reactive H₂ atmosphere compared to a N₂ atmosphere.

1. Introduction

Today, the transportation fuel supply is dominated by fossil resources, which represents 20% of the European Union's total greenhouse emissions ¹. Lignocellulosic biomass is a renewable resource that has become popular as a feedstock to convert into liquid fuels, due to its possibility to replace the liquid fossil fuel in the transportation sector. Pyrolysis of biomass is one of the most promising thermochemical conversion technologies for production of bio-oil. The bio-oil produced through traditional pyrolysis has generally a lower heating value, a higher acidity, a higher viscosity and a lower stability compared to fossil alternatives, mainly due to a relatively high content of oxygen and water ². To make bio-oil applicable as a feedstock for fuel production in existing refineries, improvement of its overall chemical and physical characteristics is necessary. The main pathway for bio-oil upgrading is deoxygenation ³, which can be performed through catalytic fast pyrolysis (CFP). The rapid heating rate of biomass in CFP enables the production of a high liquid yield, which is combined with a catalytic upgrading of bio-oil. By using certain catalysts in CFP, oxygen can be removed from the bio-oil ⁴⁻⁵. Zeolitic catalysts have been successfully employed in petroleum refineries and for methanol-to-gasoline processes. Due to the high acidity and high shape selectivity of zeolites, their potential to be used in CFP has been studied extensively in previous research ³.

One way to describe if a feedstock can be converted into hydrocarbons in an efficient way over a zeolitic catalyst, the hydrogen to carbon effective ratio (H/C_{eff} ratio), defined in equation (1), was introduced in pyrolysis studies by Chen et al. ⁶.

$$H/C_{eff} = (H - 2O)/C$$

Where H, C, and O represent the stoichiometric numbers of hydrogen, carbon and oxygen in the feedstock, respectively. Feedstocks with higher H/C_{eff} ratios are preferred for fuel production than feedstocks with lower ratios ⁶. The petroleum derivatives as feedstock gives a H/C_{eff} ratio between 1 and 2, whereas biomass feedstocks often provide a ratio up to 0.3 ⁷. In order to increase the H/C_{eff} ratio of bio-oil from CFP of biomass, the use of pyrolysis and catalytic upgrading in a H_2 atmosphere should be of interest. HZSM-5, one of the most promising zeolite catalysts investigated in catalytic pyrolysis of biomass, has a strong shape selectivity for production of aromatic hydrocarbons, which can convert the heavy oxygenated molecules into aromatic hydrocarbons by deoxygenation and aromatization of bio-oil ³.

Previous research has studied pyrolysis of biomass under atmospheric pressure of H_2 without catalysts ⁸. It has been found that a H_2 atmosphere suppresses the char yield compared to an inert atmosphere, without significant difference on the yield of pyrolytic liquids ³. It has been found that higher yields of CH_4 and CO_2 were produced from non-catalytic pyrolysis of rice husk in a fluidized bed when using H_2 as a fluidizing agent at atmospheric pressure in non-catalytic at 650°C ⁹. Previous works on biomass pyrolysis in the presence of H_2 also focus on the effect of H_2 pressure ¹⁰. It has been reported that the composition of pyrolytic liquid from pyrolysis of lignin in a microscale reactor at 650°C doesn't show significant changes at H_2 pressures lower than 1.7MPa ¹⁰. However, an increased yield of phenolics was found when increasing the H_2 pressure from 1.7MPa to 2.6MPa. This could be explained by the decomposition of larger molecular size phenolic compounds. Previous studies have also investigated fast pyrolysis of biomass over HZSM-5 in a H_2 pressure ^{8, 11-14}. For example, a recent study investigated pyrolysis of pine wood

in a Pyroprobe 5200 at 0.55MPa of H₂ atmosphere in the presence of a HZSM-5 catalyst¹⁴. It was found that higher molecular weight oxygenates in bio-oil was reduced during the pyrolysis in a H₂ atmosphere compared to a pyrolysis in an inert gas. In another study, HZSM-5 was used to in biomass pyrolysis when varying the H₂ pressure from 0.69 to 2.76MPa¹³. No significant change on the carbon yields from the major compounds in the pyrolytic vapor has been found, when increasing the pressure of H₂.

Previous studies on catalytic pyrolysis of biomass in H₂ atmosphere have been performed through analytical pyrolysis instruments, which give information mainly on composition of pyrolytic vapors. However, few studies about the product yields as well as on the consumption of H₂ have been published. Therefore, further studies on are needed in order to further study the influence of H₂ atmosphere, for example for energy and mass balance information.

Objectives of this work are to evaluate the effect of pyrolytic agents for pyrolysis of lignocellulosic biomass over HZSM-5. The effects of H₂ compared to N₂ were studied experimentally by using a bench-scale reactor. The effect of H₂ with/without HZSM-5 was evaluated by determining the composition of the liquid product, the pyrolytic gas, and the elemental compositions of the char.

2. Experimental section

2.1. Raw materials and catalysts

The raw material used was an industrially available mixture of spruce and pine with a particle size of 0.35-0.5mm provided by Svenska Cellulosa Aktiebolaget. In addition, ZSM-5 zeolite in an ammonium state with a SiO₂/Al₂O₃ ratio of 30 from Alfa Aesar was

used for the catalytic pyrolysis experiments. The catalyst acidity ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio) was chosen as 30, because it has been claimed that it gives the highest aromatic hydrocarbon yields for upgrading pyrolytic vapors from lignocellulosic biomass and limit the coke formation in presence of steam during CFP¹⁵⁻¹⁷. The catalyst was calcined in air at 550°C to achieve a protonated state. After calcination, the catalyst was pelletized, crushed, and sieved to particle sizes in the interval from 0.125 to 0.180mm.

2.2. Experimental procedure

Four experimental cases were investigated in this study in order to be able to evaluate the influence of the H_2 as pyrolytic agent on the pyrolysis process in absence/presence of the catalyst. The cases are presented in Table 1.

The pyrolysis experiments were performed in a bench-scale fixed bed pyrolyzer, illustrated in Figure 1. The system consists of a vertical steel tube with an inner diameter of 5cm, a heated zone of 60cm length and a cooled zone of 20cm. The system is further described in previous works¹⁸. Before each test, biomass was dried at 105°C for 24 hours. Thereafter, 10 grams of biomass was placed in a basket positioned in a cooled section above the furnace. Also, 10 grams of catalyst was placed as a fixed bed in the furnace prior to heating. For the non-catalytic experiments, a fixed bed of silica sand of similar particle size was used. When the furnace had reached the set temperature of 450°C, biomass was introduced to the furnace and kept in the heated zone for 25 minutes. During the experiments, carrier gas (N_2 or H_2) was set at a constant room-temperature flow rate of 130ml/min. After passing through the fixed bed, pyrolytic vapors were quenched in washing bottles placed in a cooling bath operating at -15°C. Downstream the condenser,

the permanent pyrolysis gas was collected through the water displacement method, followed by gas analysis.

For analysis of permanent pyrolysis gas, it should be noted that the flow rate of H₂ may not be constant at isothermal conditions due to reactions during pyrolysis and catalytic upgrading as well as being produced during the pyrolysis process. Therefore, only a net amount of H₂ could be calculated based on the difference of gas input and output in order to evaluate its potential net consumption/production in the pyrolyzer.

2.3. Analysis and characterization of pyrolysis products

2.3.1. Gas analysis

Gas analysis was performed with a gas chromatography (GC) instrument Agilent 490 micro-GC calibrated for CH₄, C₂H₂, C₂H₄, C₂H₆, CO, CO₂, H₂, N₂ and O₂. Also, the gas yield was measured through the water displacement method.

2.3.2. Liquid analysis

Liquid products were analyzed with a gas chromatography/mass spectrometry (GC/MS) equipment (an Agilent 7890A GC coupled with an Agilent 5975C MS). The GC program started at 40°C during a 2-minute holding time. Then, the oven was heated to 250°C at a rate of 4°C/min. Thereafter, the temperature was kept stable for 30 minutes. The atom mass unit range was set from 45 to 450. Chemstation was used together with the NIST11 library to identify the detected peaks and to calculate the peak areas.

The water content of the liquid was determined using Karl Fischer-titration and TAN-titration with standard methods ASTM E203 and ASTM D664 respectively.

2.3.3. Biomass and Char analysis

Ultimate and proximate analysis of the char and biomass were performed with methods listed in Table 2.

3. Results and Discussion

3.1. Biomass and catalyst characterization

Ultimate and proximate analysis of the biomass is presented in Table 3. Based on this, the empirical chemical formula of the biomass is $\text{CH}_{1.43}\text{O}_{0.63}$. The hydrogen to carbon effective ratio of the biomass was calculated as 0.17.

The catalyst material was characterized based on Brunauer–Emmett–Teller (BET) analysis and ICP-MS. The surface area of the catalyst was determined to be $402\text{m}^2/\text{g}$. The elemental composition of catalyst is presented in Table 4.

3.2. Product distribution

The distribution of pyrolysis products is presented in Table 5. It shows that the pyrolytic product yields have been affected by the atmospheres and catalysts. The gas yield when using a H_2 atmosphere is higher than the char yield when using a N_2 atmosphere. Similar observations based on gas production when using a H_2 atmosphere was found by Meesuk et al. and Zhang et al.^{9, 19}. They claimed that in the presence of H_2 , the char is gasified through hydrogasification pathways, and the pyrolytic vapors are decomposed and reformed extensively in H_2 atmosphere, which result in an increased gas production. This could be proved by a decreased char yield found in cases with a presence of H_2 . As expected, the gas yield is higher when using a catalyst. This is correlated to the reduced aqueous phase and non-aqueous phase yields. Simultaneously, the pyrolysis in a H_2 atmosphere shows a higher non-aqueous phase and lower aqueous phase yields compared

to cases using a N₂ atmosphere. This could be due to the H₂ increased oil yields. A higher water production was found in cases using HZSM-5. This is as expected, since more water is generated from cracking reactions, which take place on the HZSM-5 surface²⁰. The total product yield was found to be more than 100wt% of biomass in the cases when using a H₂ atmosphere. This is due to that the pyrolytic agent H₂ is being consumed and reacting with pyrolysis products during the process. The weight loss found in cases using N₂ atmospheres could be due to the coke deposition on the sand and catalyst beds.

3.3. Chemical Composition of Gas

Figure 2 shows the yields of the pyrolysis gas compounds from the investigated cases. The gas production was higher for the cases using catalytic pyrolysis, which confirms the cracking effect of HZSM-5. Furthermore, it was found that pyrolysis in a H₂ atmosphere produced increased yields of CO, CO₂, CH₄, C₂H₄, C₂H₆, and C₃H₆ in both the non-catalytic and catalytic cases compared to a N₂ atmosphere. This could be explained by the hypothesis as mentioned in section 3.2. The CO, CO₂ and hydrocarbon gases production are promoted in H₂ atmosphere, due to the secondary hydrocracking of pyrolytic vapor increases the yield of light gas molecules^{9, 19}.

A mass balance over the pyrolyzer inlet and outlet of H₂ in the case of catalytic pyrolysis in H₂ atmosphere is presented in Table 6. The result shows that the amount of consumed H₂ gas was 0.92wt% of the biomass in a non-catalytic pyrolysis and 1.01wt% of biomass in a catalytic pyrolysis. Thereby, in presence of HZSM-5, the H₂ consumption increased by 10% compared to the non-catalytic test. It indicates that H₂ is consumed during pyrolytic vapor upgrading over HZSM-5. Concerning the H₂ consumption in the pyrolysis process,

the hydrogen to carbon effective ratio of feedstock increased from 0.17 to 0.39 during a non-catalytic pyrolysis process and to 0.41 during a catalytic pyrolysis process.

3.4. Liquid analysis

Figure 3 shows the peak area distributions from the GC/MS results based on different compounds found in the non-aqueous phase. As expected, the peak area of aromatic hydrocarbons was higher in the presence of HZSM-5 than that in non-catalytic tests. Whilst in case of using a combination of both H₂ and HZSM-5, the peak area percentage of phenolics was higher than in the case of using N₂ and HZSM-5. This could be explained by a higher flow rate caused by the higher gas production when using a H₂ atmosphere, which would shorten the residence time of pyrolytic vapor on HZSM-5.

Table 7 lists the main compounds found in the non-aqueous phase in the four studied cases. Concerning the bio-oil production, hydrocarbons are some of the most desirable compounds found in these GC/MS results. It can be seen that higher peak area percentages of monoaromatic hydrocarbons (MAHs) were produced when using N₂ compared to when using H₂. Furthermore, when using a H₂ atmosphere in combination with HZSM-5, a higher concentration on polyaromatic hydrocarbons (PAHs) is found. It shows that polymerization reactions of aromatics are promoted over HZSM-5 when using a H₂ atmosphere. Two possible reason for this phenomenon could be found:

a) A spillover indicates that reactants or intermediates like H₂, O₂ and CO diffuse on the surface of a heterogeneous catalyst²¹. The spillover phenomenon of hydrogen has been studied on metal-modified ZSM-5 such as Pt/ZSM-5, Ni/ZSM-5 and Fe/ZSM-5, where the hydrogen present as H⁺ on the surface of zeolites, which could result in an increased amount of acidic site on the surface of zeolites²²⁻²⁴. Fe, Ni impurities in HZSM-5 shown

in Table 2 provides the possibility for a hydrogen spillover to take place. An increased concentration of acidic sites caused by hydrogen spillover, could promote polymerization reactions over HZSM-5 and produce more PAH during pyrolysis.

b) Deactivation of HZSM-5 caused by dealumination was observed in catalytic upgrading of high water concentration (above 50wt%) feedstock from 400°C to 500°C²⁵⁻²⁶. Vikram et al. studied the acid strength distribution of HZSM-5 under a hydrothermal treatment at 575K in different atmospheres²⁷. They observed a smaller decrease on number of acid sites on the catalysts in a H₂ atmosphere compared to an inert N₂ atmosphere, after a hydrothermal treatment. These results reveal that the H₂ atmosphere could inhibit the dealumination of HZSM-5.

In Table 8, the peak area percentage of the main compounds in an aqueous phase from two non/catalytic cases are listed. More acetic acid and less sugar peak area percentages were found when using a H₂ atmosphere compared to when using a N₂ atmosphere. It shows that more sugar breaks down to smaller oxygenates when using a H₂ atmosphere. This could be explained by the hydrocracking reaction in H₂ atmosphere mentioned in 3.3. The phenolics peak area percentages didn't show significant differences between the studied cases. The reason could be that the temperatures and H₂ pressures are not high enough for a depolymerization of lignin to take place¹⁰.

No peak value was found in the aqueous phase from the catalytic cases. The reason is thought to be the high water content in that phase. This leads to a dilution of the compounds, which result in that concentrations are below the detection limit of the instrument.

The Total Acid Number (TAN) of the liquid product from the studied four cases are shown in Figure 4. The TAN results from the cases using catalysts are much lower than the non-catalytic cases. This is expected, because the HZSM-5 could deoxygenate the organic acid to hydrocarbon compounds. The cases using H₂ have a higher total acid number than the cases using an inert atmosphere. This is true for both the aqueous phase and non-aqueous phase. This is consistent with the higher acetic acid yields from the pyrolysis process when using a H₂ atmosphere compared to when using an inert atmosphere.

3.4. Char analysis

The ultimate and proximate chemical composition of char obtained from the different experiments is presented in Table 9. The composition of char is nearly identical between the cases. Which proves that the hydrogen, provided by H₂ consumption in tests using a H₂ atmosphere, entered the liquid product. It should be noted that the lowest concentration of N in char, found in the non-catalytic test using N₂ atmosphere, could be because the composition variation of the biomass feedstock.

4. Conclusions

Catalytic and non-catalytic pyrolysis of softwood biomass experiments have been performed in a fixed bed reactor using H₂ and N₂ atmospheres. In the case of using a H₂ atmosphere, H₂ was consumed by reacting with pyrolytic vapors. This increased the H/C_{eff} ratio of the feedstock from 0.17 to 0.4. H₂ was seen to enhance the rate of polymerization reactions on HZSM-5, which could be a result of a hydrogen spillover or a H₂ inhabitation on the hydrothermal deactivation of HZSM-5. An increased gas production together with

a slightly lower char yield were found when using a H₂ atmosphere compared to when using a N₂ atmosphere. More non-aqueous liquids were produced in a H₂ atmosphere than that in a N₂ atmosphere, due to the H₂ consumption that occurred during the pyrolysis. However, the char composition is identical between four different studied cases.

Overall, the results of this study show that pyrolysis in an atmospheric pressure and using H₂ as carrier gas could increase the H/C_{eff} ratio of pyrolytic liquids during both catalytic and non-catalytic pyrolysis processes. This is highly beneficial for the applicability of bio-oil as a liquid fuel.

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Notes

The authors declare no competing financial interest.

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Table 1. Experimental cases investigated in this work.

Table 2. Methods used for biomass and char characterization

Table 3. Composition of biomass used in the fast pyrolysis experiments (db=dry basis, daf=dry ash free)

Table 4. Elemental composition of HZSM-5

Table 5. Effect of atmosphere and catalyst on product yields (wt% of biomass)

Table 6. The net amount of H₂ and consumption for the tests when using H₂ as carrier gas

Table 7. Relative peak areas of compounds identified in the non-aqueous phase of catalytic cases (presented in area%)

Table 8. Relative peak areas of compounds identified in the aqueous phase for the non-catalytic cases (presented in area%)

Table 9. Ultimate and proximate chemical composition of char (presented as wt%)

Figure 1. Schematic diagram of fixed bed system for the fast pyrolysis of biomass. 1. Gas cylinders; 2. Gas valve; 3. Electrical three heating-zone furnace; 4. Metallic rod for positioning of biomass sample; 5. Biomass in sample holder; 6. Catalytic bed; 7. Condenser; 8. Water displacement system; 9. Gas analysis equipment; 10. Cooled section.

Figure 2. Chemical compositions of the permanent pyrolysis gases in the different investigated cases (mole/10g biomass)

Figure 3. Effect of atmosphere and catalyst on the liquid product peak area percentages in the non-aqueous phase.

Figure 4. Total acid number of liquid product

Table 1. Experimental cases investigated in this work.

	H ₂	N ₂	HZSM-5
Case 1	X		
Case 2		X	
Case 3	X		X
Case 4		X	X

Table 2. Methods used for biomass and char characterization

Characteristic test	Method for char	Method for biomass
Ash content	SS 187157:1984	SS-EN ISO 18122:2015
Ash composition	-	ICP-SFMS
Volatile matter	ISO 562:2010	SS-EN ISO 18123:2015
Elemental composition (C, H, N)	ASTM D5373:2013/ ISO 29541:2010	SS-EN ISO 16948:2015
Elemental composition (Cl, S)	-	SS-EN ISO 16994:2016
Heating value	-	SS-EN 14918:2010

Table 3. Composition of biomass used in the fast pyrolysis experiments (db=dry basis, daf=dry ash free)

Moisture [wt%]	105°C	2.5	
Volatile Matter [wt%, db]		83.6	
Ash [wt%, db]		<0.30	
HHV (daf) [MJ/kg]		19.190	
Ultimate Analysis [wt% db]			
C		50.4	
H		6.1	
O		43.2	
N		0.10	
Cl		<0.01	
S		<0.012	
Metals [mg/kg db]			
Si	23.1	Pb	0.728
Al	6.83	B	1.58
Ca	409	Cd	0.048
Fe	8.81	Co	0.0325
K	216	Cu	3.19
Mg	58.9	Cr	0.157
Mn	51.2	Hg	<0.01
Na	8.53	Mo	0.00963
P	15.5	Ni	2.51
Ti	0.36	V	<0.01
As	<0.1	Zn	8.5
Ba	5.32		

Table 4. Elemental composition of HZSM-5

Element	Concentration (mg/kg)
Si	340000
Al	21200
Fe	<700
Ni	62.1

Table 5. Effect of atmosphere and catalyst on product yields (wt% of biomass)

Case	H ₂	H ₂ / HZSM-5	N ₂	N ₂ / HZSM-5
Char	25.30	25.07	25.77	25.63
Organic compounds in non-aqueous phase	12.24	10.80	9.68	9.43
Organic compounds in aqueous phase	23.43	9.71	23.99	7.84
Water production	23.11	31.45	24.36	35.06
Gas	18.35	25.23	12.15	17.67
Total	102.43	102.27	95.95	95.63

Table 6. The net amount of H₂ and consumption for the tests when using H₂ as carrier gas

	H ₂ input (L)	H ₂ output(L)	H ₂ consumption (wt% of biomass)	H/C _{eff}
H ₂	3.25	2.22	0.92	0.39
H ₂ /HZSM-5	3.25	2.12	1.01	0.41

Table 7. Relative peak areas of compounds identified in the non-aqueous phase of catalytic cases (presented in area%)

Compound	H2	N2	H2 HZSM5	N2 HZSM5
Monoaromatic Hydrocarbons	-	-	42.34	62.23
Benzene			2.53	6.37
Toluene			13.72	24.18
Ethylbenzene			0.75	1.01
p-Xylene			14.26	18.83
Benzene, 1,3-dimethyl-			3.93	4.86
Benzene, 1-ethyl-3-methyl-			0.49	0.53
Benzene, 1-ethyl-2-methyl-			0.37	0.43
Mesitylene			0.49	0.45
Benzene, 1,2,4-trimethyl-			2.66	2.85
Benzene, 1,2,3-trimethyl-			0.22	0.00
Indane			1.04	1.10
Benzene, 1-propynyl-			0.61	0.70
2-Methylindene			0.77	0.74
1H-Indene, 2,3-dihydro-4,7-dimethyl-			0.10	0.00
Benzene, (1-methyl-2-cyclopropen-1-yl)-			0.38	0.19
Polyaromatic Hydrocarbons	-	-	43.59	32.48
Naphthalene			9.42	7.64
Naphthalene, 2-methyl-			13.62	11.51
Naphthalene, 1-methyl-			4.65	3.66
Naphthalene, 2-ethyl-			0.90	0.76
Naphthalene, dimethyl- & trimethyl-			12.61	7.72

Fluorene			0.10	0.00
Anthracene			0.22	0.00
Phenanthrene			0.95	0.54
Phenanthrene, 2-methyl-			1.12	0.64
Phenolics	84.80	87.49	10.94	5.29
Phenol, 2-methyl-	2.02	1.54	0.58	0.23
Phenol, 2-methoxy-	14.53	12.78	1.87	1.09
Creosol	25.20	24.17	3.20	2.39
Phenol, 4-ethyl-2-methoxy-	10.05	11.51	1.47	0.99
2-Methoxy-4-vinylphenol	9.83	9.11	1.23	0.38
Eugenol	2.93	3.34	0.36	0.00
Phenol, 2-methoxy-4-propyl-	2.93	3.52	0.31	0.00
trans-Isoeugenol	2.82	3.30	1.92	0.22
Phenol, 2-methoxy-4-(1-propenyl)-	17.42	18.22		

Table 8. Relative peak areas of compounds identified in the aqueous phase for the non-catalytic cases (presented in area%)

Compound	H2	N2
Acetic acid	9.10	3.42
Phenolics	20.08	13.29
Phenol, 2-methoxy-	7.75	3.69
Creosol	9.40	4.58
trans-Isoeugenol	2.93	2.65
Apocynin	0.00	2.37
Sugars	58.30	77.43
.beta.-D-Glucopyranose, 1,6-anhydro-	5.87	8.74
D-Allose	52.43	68.69

Table 9. Ultimate and proximate chemical composition of char (presented as wt%)

	H ₂	H ₂ with HZSM-5	N ₂	N ₂ with HZSM-5
Ash	0.80	0.90	1.10	0.80
Volatile matter	27.60	26.90	27.30	26.50
C	81.80	81.70	82.10	82.00
H	3.40	3.40	3.40	3.40
N	0.28	0.27	0.11	0.22
O	13.72	13.73	13.29	13.58

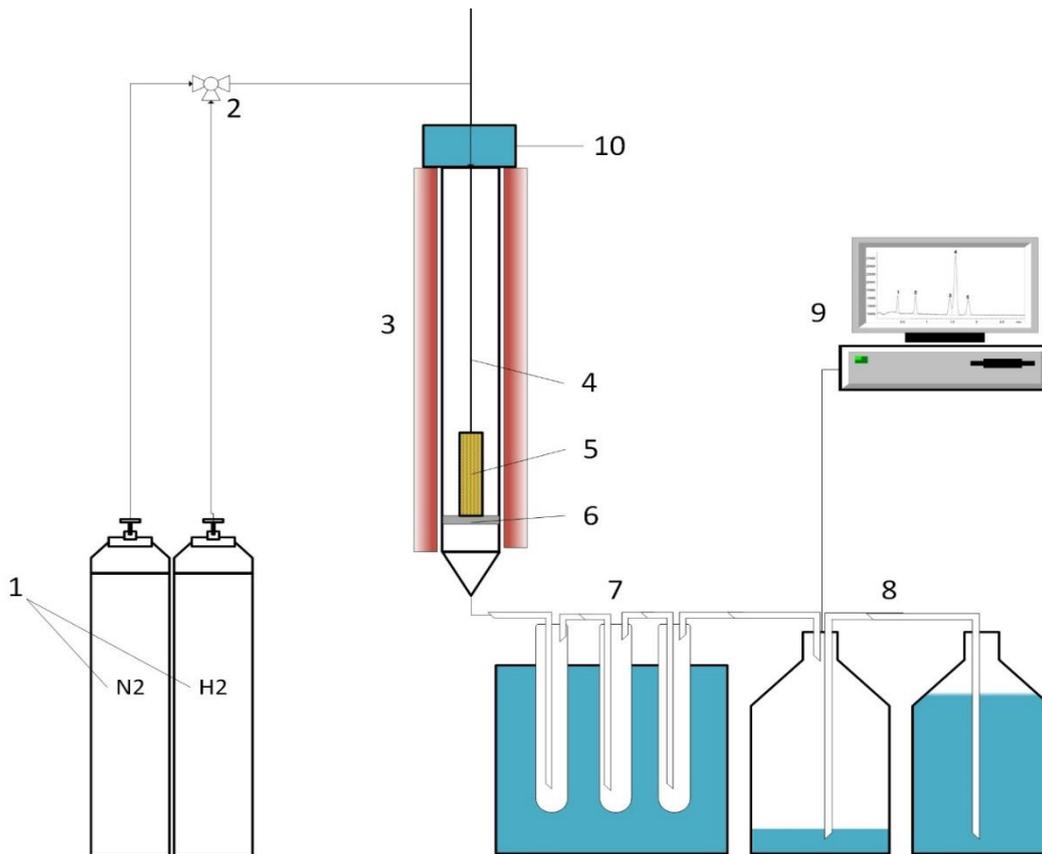
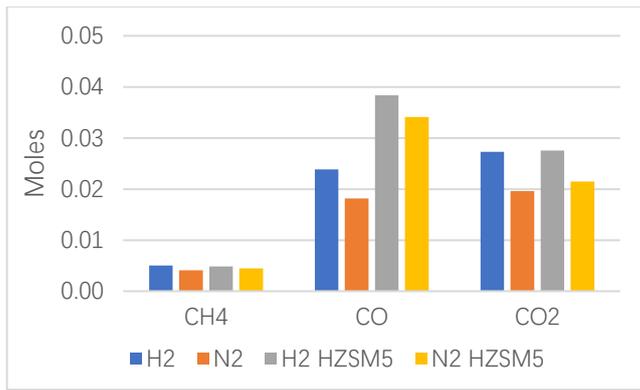
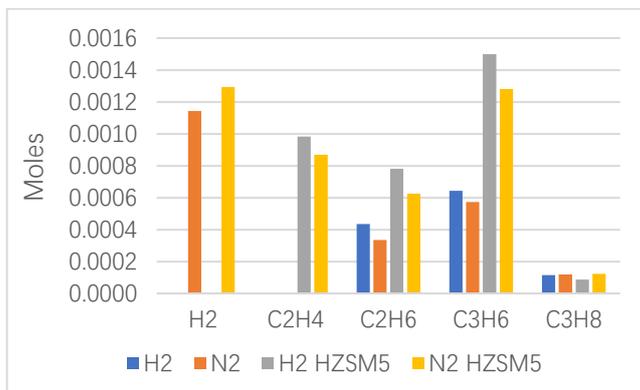


Figure 1. Schematic diagram of fixed bed system for the fast pyrolysis of biomass. 1. Gas cylinders; 2. Gas valve; 3. Electrical three heating-zone furnace; 4. Metallic rod for positioning of biomass sample; 5. Biomass in sample holder; 6. Catalytic bed; 7. Condenser; 8. Water displacement system; 9. Gas analysis equipment; 10. Cooled section.



(a)



(b)

Figure 2. Chemical compositions of the permanent pyrolysis gases in the different investigated cases (mole/10g biomass)

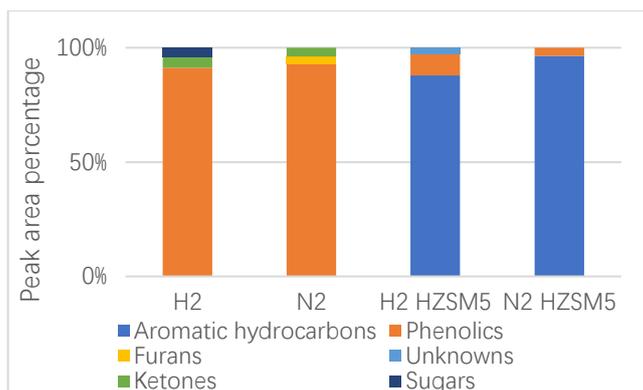


Figure 3. Effect of atmosphere and catalyst on the liquid product peak area percentages in the non-aqueous phase.

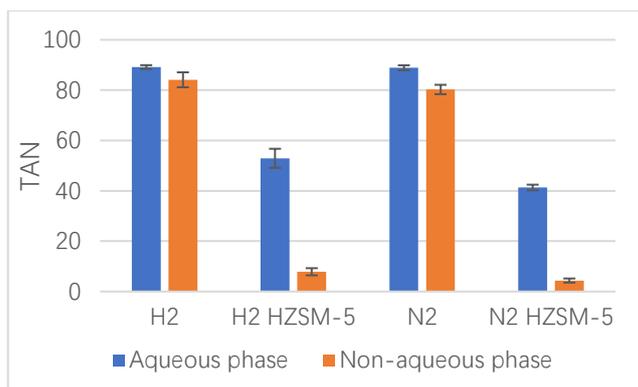


Figure 4. Total acid number of liquid product