1 Upgrading pine sawdust pyrolysis oil to green biofuels by HDO over

2 zinc-assisted Pd/C catalyst

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35 Abstract: Upgrading pyrolysis oil by hydrodeoxygenation (HDO) is a promising route for the

36 production of advanced biofuels. The proper reaction conditions and catalysts are important for the

37 success of this process. Previously our research group investigated the ratio of Zn and Pd on the

38 synergistic effect for HDO bio-oil upgrading. This present research focuses on determining the optimal

reaction conditions for HDO conversion of pyrolysis oil produced from pine sawdust. Temperatures of 150, 200 and 250 °C and hydrogen pressures of 1.38, 2.76 and 4.14 MPa were evaluated. Syngas, liquids and coke were the primary products evaluated. Syngas was characterized using a Gas chromatography (GC). The liquids were characterized using a Gas chromatography-mass spectrometry (GC-MS). Increasing reaction temperature resulted in increased coke yields. Treatment at 250 °C and 1.38 MPa resulted in the highest hydrocarbon content (6.06%). The treatment at 200 °C and 1.38 MPa produced the largest amounts of hydrocarbons in C₆-C₁₂ range (5.07%). The physicochemical characterizations further support the GCMS results. Syngas analysis revealed that higher hydrogen pressure leads to increased hydrogen consumption and results in more oxy-compounds conversion to hydrocarbons. The syngas analysis also supports the liquid analysis result.

Keywords: Hydrodeoxygenation; Pyrolysis oil; Upgrading; catalyst; Pd/C; Zn²⁺

1. Introduction

Climate concerns, depletion of petroleum reserves, and energy security have created the need to replace fossil fuels with renewable energy sources[1-3]. Carbon dioxide produced by burning fossil fuels is a major cause of global warming [4]. Biomass, a renewable energy resource, is widely considered to be one of the most promising alternatives to conventional fuels [5]. It has low sulfur and nitrogen content, high energy value, and a CO₂ balance of almost zero[1, 2]. Conversion of the widely distributed biomass to biofuels is an opportunity to reducing greenhouse emissions and improving energy security [6].

Pyrolysis thermal conversion of biomass in the absence of O₂ is one of the most promising thermal conversion technologies. Initial research reveals that raw bio-oils produced by pyrolysis result in low

heating values, high acidity and water content, high viscosity and molecular instability. These are major hurdles that must be overcome before pyrolysis produced bio-oil can be effectively used. To overcome these hurdles pyrolysis oil must be upgraded. This requires catalytic pyrolysis [7, 8], HDO [9, 10], catalytic cracking [1, 2], emulsification with biodiesel [11] and catalytic esterification [12]. HDO has attracted some attentions because of deoxygenation resulting in increased hydrocarbons content. Commonly evaluated catalysts include Pt/Al₂O₃ [13], Pd/C [14], Ni₂P/SAPO-11 [15], Ru/C [16] and Ru/H-Beta [17]. The HDO process requires a high pressure hydrogen (generally >6.89 MPa (1000 psi)), making the process unsafe and costly. A less expensive and more efficient approach must be found.

Recently, the synergistic interaction between Pd and Zn catalysts has attracted attention. Pd enhances the catalyst performance and improves the HDO reaction efficiently. [18] However, most of research to date has used simulated bio-oil in HDO processes for the reaction mechanism [18, 19]. Our research group previously inspected the synergistic effect of Zn/Pd/C on the upgrading of bio-oil produced from pyrolysis of pine sawdust. This research determined the optimal reaction temperature and hydrogen pressure for HDO upgrading. Temperature has a large influence on the performance of the active sites in and on the catalyst [20]. A hydrogen-rich atmosphere aids the removal of oxygen from the bio-oil [21]. This current research was initiated to find the optimal reaction temperature and hydrogen pressure for upgrading pyrolysis produced bio-oil from pine saw dust using a Zn/Pd/C catalyst. Temperatures of 150, 200 and 250°C and hydrogen pressures of 1.38, 2.76 and 4.14 MPa were used.

2. Experimental

2.1 Materials

ZnCl₂, 99.99 wt. %, and Pd/C, 5.00 wt. % were purchased from Aldrich and used as received. The raw pine sawdust bio-oil was obtained from a proprietary pyrolysis pilot reactor which is comprised of a screw feeder, a reaction chamber and multiple condensers. The pine saw dust was feed into the reactor at a rate of 1.36 kg/h. The temperature of the reaction chamber was set at 538 °C (1000 °F). The temperature of the condensers were set at -10 °C. The pyrolysis pilot reactor is located in the Advanced Biofuel Laboratory located in the Agricultural & Biosystems Engineering Department at South Dakota State University.

2.2 General experimental procedure

A typical experiment consisted of raw bio-oil (50.00 g), 5.00 wt. % of Pd/C (5.00 g, 2.40 mmol Pd) and ZnCl₂ (0.63 g, 4.64 mmol) being added to a stainless steel high pressure reactor (500 mL, Parr, Model 4575). The reactor was weighted and subsequently sealed. The air in the high pressure reactor was purged by injecting H₂ up to a pressure of 3.45 MPa and subsequently releasing the pressure back down to 0 MPa. This purging was repeated three times. The system was then pressurized using H₂ to a final pressure of 1.38, 2.76 and 4.14 MPa. The reactor was heated up the temperature of 150, 200 and 250°C. The treatments evaluated were Case 1, 150 °C at 1.38 MPa, Case 2, 150 °C at 2.76 MPa, Case 3, 150 °C at 4.14 MPa, Case 4, 200 °C at 1.38 MPa, Case 5, 200 °C at 2.76 MPa, Case 6, 200 °C at 4.14 MPa, Case 7, 250 °C at 1.38 MPa, Case 8, 250 °C at 2.76 MPa and Case 9, 250 °C at 4.14 MPa. The mixture was heated at a rate of 5 °C/min to reach the desired treatment temperature. This treatment temperature was maintained for 4 hours. The treatment mixture was stirred at a speed of 1000 rpm for the entire experiment. Upon experiment completion the heat was removed and the reaction vessel was cooled to room temperature. The mixture was filtered to remove the Pd/C catalyst and coke. The reaction mixture was washed with MeOH and dried at 30 °C. The filtrate was collected and

diluted in a volumetric flask. All samples were sent to Chemistry Department, South Dakota State University for GC-MS analysis. The yields of char, oil and gas were calculated according to the following equations developed by Joon Weon Choi [22].

$$\text{Yield of gas} = [\text{Liquid2} - \text{Liquid1} - (\text{Solid2} - \text{Solid1})] / \text{Liquid1} * 100\%$$

$$\text{Yield of coke} = (\text{Solid2} - \text{Solid1}) / \text{Liquid1} * 100\%$$

$$\text{Yield of liquid} = 1 - \text{Yield of gas} - \text{Yield of coke}$$

Where:

Liquid1 = the mass of liquid product before treatments

Liquid2 = the mass of liquid product after treatments

Solid1: the mass of catalyst added into the reactor

Solid2: the mass of solid residue after being washed and dried

2.3 Product characterization

The water contents of samples were measured using a Karl Fischer Titrator V20 (Mettler Toledo Company). Dynamic viscosity was measured at 20 °C using a viscosity analyzer (REOLOGICA Instruments AB Company Dynamic Viscosity). The total acid number (TAN) of bio-oil was measured using a Micro TAN Titirator (GR Scientific Ltd) at room temperature. The HHV was measured using a bomb calorimeter (Parr Instrument Company 1341). Syngas was analyzed using a GC equipped with a TCD and a FID. Standard gas mixtures were used for calibration, and argon was used as the carrier gas. GC-MS (Agilent GC-7890A (DB-5 column: 30 m × 0.25 mm × 0.25 μm) and MSD-5975C (Electron

ionization at 70 eV, mass range of 50-5000 m/z, semi-quantitation based on TIC, mass chromatograms)) were used to analyze the chemical composition each sample. The gas chromatograph was programmed at 60 °C for 1 min, followed by ramp 1 at 3 °C/min to 260 °C and ramp 2 at 5 °C/min to 280 °C. The temperature was held for an additional 10 minutes after each ramp. The injector temperature was 300 °C, and the injection size was 1 µL. The flow rate of the carrier gas (hydrogen) was 1 mL/min. The compositions were identified using the NIST Mass Spectral Library and literature values [1, 2].

In order to obtain objective experiment results, each test was performed in duplicate. All observations were recorded in triplicate and average values were reported.

3. Results and discussion

3.1 Product Distribution

A series of HDO experiments we completed to investigate the effect of reaction temperature and pressure on the effectiveness of Pd/Zn catalysis to upgrade pyrolysis produced bio-oil. After each test, the HDO products-gas, upgraded bio-oil and coke collected and analyzed. The catalyst used for each experiment was Zn/Pd on an activated carbon-support. Table 1 shows the mass of gas, liquids ad coke produced from each treatment. The formation of solid residue or coke increased with increased temperature. This suggests that the high temperatures induced polymerization and polycondensation reactions. The coke could be formed on the surface of the carbon-supported catalyst [23]. There was not a significant difference in the coke produced from each experiment. The liquid products during catalytic HDO reactions consisted of two phases, an aqueous phase and an oil phase. The aqueous phases contained primarily water and a few organic compounds. The oil phase consisted of primarily

organic compounds such as acids, esters, phenols, aldehydes, alcohols, ketones, ethers, hydrocarbons. The oil phase yields varied from 40.28% to 46.72%. The gas yields varied from 11.57% to 18.31%. The different treatment temperatures and hydrogen pressures could result in different product distribution.

3.2. Physicochemical properties

Hydrodeoxygenation results in hydrogenation and deoxygenation reactions, which improve bio-oil quality. Usually, parameters such as higher heating value, viscosity, water content and total acid number are used to evaluate the physicochemical properties of up graded bio-oil. These parameters are presented in Table 2. The raw bio-oil (case 0) was homogeneous, meaning no aqueous phase and oil phase separation. The bio-oil in Case 0 represents the raw bio-oil resulted from pyrolysis without HDO process upgrading. Therefore, all physicochemical properties parameters are presented on a total basis. The liquid products produced during Case 1 – Case 9 catalytic upgrading treatments resulted in an aqueous phase and an oil phase. The combustion performance of biofuels in engines can be significantly affected by the water content in bio-oils [23]. Compared to the raw bio-oil, the HDO upgraded bio-oil resulted in higher total water contents. This was the result of catalytic supported deoxygenation reactions. One hydrogen molecule consumes an oxygen atom from the oxygenated compounds, resulting in a direct conversion to water. The highest water content was 34.08 %. It was from the treatment of 250 °C at 4.14 MPa (Case 9). High temperature and high pressure increased dehydration. Case 6 (200 °C at 4.14 MPa) and Case 9 (250 °C at 4.14 MPa) resulted in low water levels (7.92%, 9.09%) in the oil phase. This trend indicates that the oil phases obtained under Case 6 (200 °C at 4.14 MPa) and Case 9 (250 °C at 4.14 MPa) treatment conditions produced larger amounts of hydrophobic compounds.

Viscosity measurement results revealed reaction conditions had a large effect on the viscosity of the upgraded bio-oil. The raw pyrolysis oil had the lowest viscosity (0.01 Pa•s) due to the homogeneity of the oil water mixture and the fact the water content was high. Increasing the reaction temperature and hydrogen pressure resulted in reduced bio-oil viscosity. This suggests that some breakdown of higher molecular-weight structures occurred, which is consistent with the Yaseen Elkasabi's research result. [9] The water content of the liquid oil increased from 24.55 wt. % in the raw bio-oil (Case 0) to more than 26.79 wt. % in those samples that were catalytically upgraded. This indicates that the composition of the bio-oil was changed by deoxygenation and dehydration. Total acid number (TAN) shows the amount of Brønsted acids present in the sample on an absolute basis. Hence, the TAN indicates the corrosiveness of the sample. [9] Total acid number measurement is much more relevant for measuring acidity. Most of the acidity comes from the presence of acetic acid. Carboxylic acids, phenols and other acidic compounds can have a significant contribution. Raw pyrolysis oil's total acid number was 998.05 mg KOH/g. Most treatments resulted in a reduction of the total acid number. Case 1 produced the lowest TAN. When compared to the raw pyrolysis oil, the TAN value by treatments (Case 1,2,3,4 and 7) decreased. However, The TAN value of treatment Case 5,6 and 9 were higher than the raw bio-oil. In each case, some amounts of big molecules were unzipped into small ones. The processes obtained the big acid molecules such as Propanoic acid-2-methyl-heptyl ester, Isobutyl 2,5,8,11-tetraoxatridecan-13-yl carbonate, 13,14-Dihydroabietic acid and 13Alpha-delta(8)-dihydroabietic acid. These acid components did great contributions to the TAN value. The increased TAN compared to that of the pyrolysis oil might be due to these big acid molecules. The heating value of raw bio-oil by (Case 0) was 14.81 MJ/kg. This was significantly lower than the catalyst treated bio-oil listed in Table 2. It was due to the high water content of the homogenous bio-oil

mixture. The catalytic treated bio-oil produced higher heating values than the raw bio-oil. This is due to the lower oxygen content of the oil phase the catalytically treated bio-oil. The highest HHV (28.41 MJ/kg) of the oil phase was achieved using treatment Case 9.

3.3 Influence of treatments on bio-oils

Bio-oil is a complex highly oxygenated organics mixture originating from the degradation of pine saw dust cellulose, hemicellulose and lignin [24]. The organic compounds in this mixture consists of esters, ethers, aldehydes, ketones, phenols, organic acids and alcohols according to the function groups. [25] Upgraded bio-oil, the target product in this study, is a dark brown and homogeneous liquid having a smoky odor. The hydrocarbon component of biofuels is the most important component. Hydrocarbons in the range of gasoline can be obtained by upgrading the bio-oil.

GC-MS measurements can capture only a small portion of the chemical identities present in biofuels. Small and large molecular weight compounds undergo the same phenomena in GC-MS. The GC-MS analysis can provide a reliable approach to assessing the HDO products created. In this work, the GC-MS was employed to analyze all resulting bio-oils. The compound composition of the samples evaluated having a great than 5% relative concentration are displayed in Tables 3.

The hydrogen pressure of the HDO process plays a key role on the distribution of the final components in upgraded bio-oil. As part of this research the reaction pressure was varied to provide a close inspection on the influence of hydrogen pressure on the conversion of oxygenated compounds and final product distribution. All upgraded bio-oils contain almost the same compounds. These include propanoic acid, 2-methyl-propanoic acid heptyl ester, octadecanoic acid, dehydroabiatic acid, 13alpha-delta(8)-dihydroabiatic acid, methyl stearate-methyl pyruvate dimethyl acetal, methyl

dehydroabietate, catechol, phenol, 4-methyl-1,2-benzenediol, creosol, 2-methyl-phenol, 4-ethylcatechol, 2,4-dimethyl Phenol, 1-hydroxy-2-butanone, acetoin, cyclopentanone et al. This similar composition of treated bio-oils implies there were similar transformation pathways for typical compounds.

HDO and catalytic treatment can increase hydrocarbon content when compared to the pine sawdust pyrolysis untreated raw bio-oil (case 0), Table 3. Higher temperatures and higher hydrogen pressure increase the hydrocarbons content of the upgraded bio-oils treated with Zn/Pd/C catalyst. The high hydrogen pressure resulted in increased hydrogen solubility in the liquid bio-oil during the HDO process. The hydrogen-rich atmosphere in the liquid oil caused the catalyst to be more reactive [26, 27]. At the same temperature level, increasing hydrogen pressure did not increase the hydrocarbons content as evidenced in Case 1-3 and in Case 4-6. Case 7 (250 °C at 1.38 MPa) resulted in the production of the highest hydrocarbon content (6.06%). Case 4 (200 °C at 1.38 MPa) obtained the second highest hydrocarbon content. The upgraded bio-oil produced using treatment Case 4 (200 °C at 1.38 MPa) achieved the highest amounts of hydrocarbons in C₆-C₁₂ fraction (5.07%). This fraction could be directly used as gasoline. Treatment Case 4, 7 and 9 producing the higher hydrocarbons contents resulting in this upgraded bio-oil having the higher HHV.

The ZnCl₂ was added to the mixture of the Pd/C and substrates. The Pd/C was picking up the Zn²⁺ from the solution. The synergistic effect between Zn(II) and Pd can be built up without formation of a Zn-Pd alloy [18, 19].

It is worth noting that all catalytic treatments (Case 1-9) resulted in the elimination of aldehydes in the upgraded bio-oil. The aldehyde groups could be selectively deoxygenated by Zn/Pd/C catalyst. The

occurrence of Zn^{2+} made the deoxygenation process of the C=O group more efficiently. Aldehyde compounds including glycolaldehyde dimethyl acetal and hexanal dimethyl acetal were completely converted during upgrading. Abu-Omar and coworkers have also obtained a similar result [19].

All treatments effectively converted alcohols. The alcohols content (6.81%) in the raw pyrolysis oil was decreased to a trace amount in Case 8 (250 °C at 2.76 MPa). The Zn^{2+} ions can activate the substrate via binding to the OH group and inducing reactivity on the surface with Pd-H. In that way, the introduction of Zn^{2+} significantly increases the Pd/C HDO capacity.

3.4 The influence of experimental treatments on syngas

Following the HDO reactions, the gas products were collected and analyzed. The gaseous products contained H_2 , CO , CO_2 , CH_4 , C_2H_4 , C_2H_6 , C_3H_6 , C_3H_8 , C_4H_8 and C_4H_{10} . The initial pressure was the hydrogen pressure at the beginning of the experiment at room temperature. The final pressure is the pressure displayed on the piezometer after the reactor has cooled down to room temperature. In order to record the actual pressures during the reaction, the maximum pressure is listed for each treatment performed. The volume content of gas components and pressure information are displayed in the Table 4.

The initial pressure and final pressure in the reactor were different. This demonstrates that hydrogen was consumed during which HDO processes was carried out over the Zn/Pd/C catalyst. Note that high reaction temperature experiments that began at the same initial pressure ended up with lower final pressures. This indicates that the increasing temperature resulted in increased hydrogen consumption. High hydrogen pressure resulted in increased hydrogen consumption resulting in increased oxy-compounds conversion to hydrocarbons. The gas analysis also supports the liquid analysis.

251 4. Conclusions

252 This research was initiated to determine the optimal reaction conditions of temperature and
253 hydrogen pressure for converting pyrolysis generated pine saw dust oil to upgraded bio-oil.

254 Temperatures of 150, 200 and 250 °C and hydrogen pressures of 1.38, 2.76 and 4.14 MPa were
255 evaluated. Increasing reaction temperature resulted in increased coke yield. The results showed that
256 the treatment at 250 °C and 1.38 MPa produced the highest hydrocarbon content (6.06%). The
257 treatment at 200 °C and 1.38 MPa produced the highest amounts of hydrocarbons in the C₆-C₁₂ range
258 (5.07%). Syngas analysis indicates that high initial hydrogen pressure resulted in more oxy-compounds
259 conversion and increased hydrocarbons production.

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335 **Table 1** The products distributions of gas, liquid and coke

Treatments	Gas (%)	Liquid (%)		Coke (%)
		Aqueous phase	Oil phase	
Case 1	11.62±3.09	44.25±2.71	43.91±0.44	0.22±0.06
Case 2	17.02±1.28	40.17±0.24	42.54±1.00	0.27±0.04
Case 3	18.31±1.69	39.14±6.30	42.26±4.57	0.29±0.04
Case 4	17.46±1.43	39.88±0.49	42.33±1.90	0.33±0.01
Case 5	11.98±1.44	41.95±1.34	45.79±0.14	0.29±0.04
Case 6	14.44±0.70	40.57±4.85	44.65±5.60	0.35±0.04
Case 7	17.48±2.16	41.13±2.49	40.99±0.31	0.40±0.02
Case 8	11.57±0.01	41.30±2.80	46.72±2.85	0.41±0.04
Case 9	16.68±1.60	42.65±2.01	40.28±3.51	0.39±0.10

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344 **Table 2** The properties of upgraded bio-oils

Treatments	HHV (MJ/kg)	Viscosity	Water content			TAN
		(Pa•s)	(Wt. %)			(mg KOH/g)
		OP	AP	OP	Total	OP
Case 1	25.99	16.80	46.08	21.19	29.69	300.10
Case 2	26.22	6.50	47.99	17.65	26.79	590.05
Case 3	26.73	25.85	55.83	13.05	27.37	542.30
Case 4	28.19	0.68	64.65	11.01	30.44	731.47
Case 5	27.47	0.36	65.65	11.77	32.93	1503.30
Case 6	25.16	0.61	64.59	7.92	29.74	1245.75
Case 7	27.49	0.21	63.35	11.44	30.75	731.47
Case 8	25.85	0.01	66.47	11.46	32.81	2706.30
Case 9	28.41	0.47	71.33	9.09	34.08	691.00

345 Note: 1. The raw bio-oil (case 0) was homogeneous without an aqueous phase and an oil phase. Its
346 total higher heating value was 14.81 MJ/kg. Its viscosity was 0.01 Pa•s. Its total water content was
347 24.55 wt. %. Its total acid number was 998.05 mg KOH/g. 2. All bio-oils treated (case 1-9) had two
348 phases-an aqueous phase (AP) and an oil phase (OP).

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351 **Table 3** Chemical composition of the bio-oils

Compounds	Molecular formula	Relative content (%)									
		Case 0	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6	Case 7	Case 8	Case 9
Acids		1.73	9.69	19.7	3.39	8.36	4.54	8.36	3.91	6.31	11.7
				3							0
Acetic acid	C ₂ H ₄ O ₂			3.71							7.89
Propanoic acid	C ₃ H ₆ O ₂	1.04				2.28			1.76	0.70	0.75
Lactic acid	C ₃ H ₆ O ₃							1.49			
Propanoic acid, 2-methyl-	C ₄ H ₈ O ₂							0.69	0.51		
Butanoic acid, 4-hydroxy-	C ₄ H ₈ O ₃							0.69		0.93	0.61
Homovanillic acid	C ₉ H ₁₀ O ₄			1.14				1.28			

2-t-Butyl-4-methyl-5-oxo-[1,3]dioxolane-4-carboxylic acid	$C_9H_{14}O_5$	0.69				
Butanoic acid, 2,3-dimethyl-2-(1-methylethyl)-	$C_9H_{18}O_2$		0.59	1.02		
Chrysanthemic acid	$C_{10}H_{16}O_2$	0.65		0.55		
3-Decanoync acid	$C_{10}H_{20}O_2$				0.60	
3-Hydroxydecanoic acid	$C_{10}H_{20}O_3$	1.06				
Propanoic acid, 2-methylheptyl ester	$C_{11}H_{22}O_2$		0.75	1.14	1.08	0.91

Isobutyl	$C_{14}H_{28}O_7$	5.27									
2,5,8,11-tetr											
aoxatrideca											
n-13-yl											
carbonate											
Octadecanoi	$C_{18}H_{36}O_2$	2.15	2.04		1.51	0.92	1.43		1.61	1.03	
c acid											
Dehydroabi	$C_{20}H_{28}O_2$	4.36	2.40	1.95	2.63	0.91		1.64	2.47	0.51	
etic acid											
13,14-Dihyd	$C_{20}H_{20}O_2$						1.17				
roabietic											
acid											
13Alpha-del	$C_{20}H_{20}O_2$	3.18	3.46	1.44	0.60		0.53				
ta(8)-dihydr											
oabietic acid											
Esters		4.23	3.17	1.90	9.28	2.92	6.19	3.67	3.39	3.14	4.53
Formic acid,	$C_6H_{12}O_2$							2.35		1.14	2.68
3-methylbut											
-2-yl ester											
Methyl	$C_6H_{12}O_4$		0.94	0.73		0.89	0.52			0.69	

pyruvate

dimethyl

acetal

2,5-Furandi $C_6H_6O_3$

0.66

one,

3,4-dimethyl

-

2-Ethoxyeth $C_8H_{16}O_3$

0.61

yl

isobutyrate

Benzoic $C_9H_{10}O_4$ 0.96

acid,

4-hydroxy-3

-methoxy-,

methyl ester

Butyl $C_9H_{18}O_4$

2.33

2-(2-methox

yethoxy)ace

tate

Carbonic $C_{10}H_{12}O_4$

0.90

acid,

2-methoxye

thyl phenyl

ester

Acetic acid, $C_{10}H_{18}O_3$

0.73

2-propyltetr

ahydroxyra

n-3-yl ester

Acetic acid, $C_{10}H_{20}O_2$

1.11

3-methylhe

pt-3-yl ester

Ethyl $C_{11}H_{14}O_4$

0.96

0.95

homovanilla

te

Benzeneace $C_{12}H_{16}O_2$

0.62

tic acid,

2-methylpro

pyl ester

Butanoic $C_{13}H_{26}O_2$

0.60

1.19

acid,

2-methyl-,

octyl ester

2,3,4,6-Tetr $C_{14}H_{20}O_{10}$ 3.27

α -O-acetyl-D

-glucopyran

ose

Diisobutyl $C_{14}H_{26}O_7$ 1.48 2.47

(oxybis(etha

ne-2,1-diyl))

dicarbonate

Oxalic acid, $C_{17}H_{24}O_4$ 0.80

hexyl

2-isopropylp

henyl ester

Methyl $C_{19}H_{38}O_2$ 0.55 0.56 0.54 0.50

stearate

Octadecanoi $C_{20}H_{40}O_3$ 1.33 0.65 1.11

c acid,

2-hydroxyet

hyl ester

Methyl dehydroabie tate	C ₂₁ H ₃₀ O ₂	1.09	0.96	0.94	1.09	0.73	0.80	0.83	0.61	0.55	
Phenols		14.9	16.0	19.8	14.1	19.7	14.9	15.9	16.2	13.5	12.3
		9	3	7	6	9	3	3	5	8	2
Maltol	C ₆ H ₆ O ₃	0.63									
Catechol	C ₆ H ₆ O ₂	3.09	2.51	1.59	1.79	1.70	1.70	1.67	1.25	1.09	0.93
Phenol	C ₆ H ₆ O	0.60	1.01	1.56		1.52		1.66	0.51	0.71	0.73
1,2-Benzene diol, 3-methyl-	C ₇ H ₈ O ₂	0.74									
1,2-Benzene diol, 4-methyl-	C ₇ H ₈ O ₂	1.63	0.73	1.11	0.61	0.56	0.56	1.06	0.67	0.67	
Mequinol	C ₇ H ₈ O ₂		0.51								
Creosol	C ₇ H ₈ O	1.91	2.23	2.82	2.37	2.49	2.04	1.97	2.02	1.65	1.58
p-Cresol	C ₇ H ₈ O		0.94	1.31	0.78		1.31	1.11	0.80	0.96	
Phenol, 2-methyl-	C ₇ H ₈ O	1.08	0.60	1.25		1.10	0.83	0.75	0.70	0.59	0.61

Alcohols		6.81	0.91	1.16	4.86	2.03	3.08	4.81	2.14	-	0.91
Propylene	$C_3H_8O_2$							0.59			0.91
Glycol											
Glycerin	$C_3H_8O_3$	1.59						1.18	0.68		
Cyclopentanol	$C_5H_{10}O$	0.94									
2-Furanmetha	$C_5H_{10}O_2$				1.03						
nol,											
tetrahydro-											
3-Pentanol	$C_5H_{12}O$						1.88				
2-Butanol,	$C_5H_{12}O_2$							1.98			
1-methoxy-											
Ribitol	$C_5H_{12}O_5$								0.52		
Xylitol	$C_5H_{12}O_5$								0.94		
.beta.-D-Gluco	$C_6H_{10}O_5$	3.16									
pyranose,											
1,6-anhydro-											
3,4-Altrosan	$C_6H_{10}O_5$	1.12									
D-Fucose	$C_6H_{12}O_5$					1.19					

3-Pentanol,	C ₆ H ₁₄ O	0.64	1.06
2-methyl-			
1,3-Dioxane-5-	C ₇ H ₁₃ O ₃		0.84
methanol,			
4,5-dimethyl-			
1,3-Dioxan-5-	C ₇ H ₁₇ O ₃	3.83	
ol,			
4,4,5-trimethy			
l-			
2,4,4-Trimethy	C ₈ H ₁₈ O	0.52	
l-1-pentanol			
2-Cyclohexen-	C ₉ H ₁₆ O		0.63
1-ol,			
3,5,5-trimethy			
l-			
1-Propanol,	C ₁₀ H ₁₄ O ₂		0.57
3-(phenylmet			
hoxy)-			
Dihydro-isoste	C ₂₀ H ₃₂ O ₃	0.91	
viol methyl			

ester										
ketones										
		4.42	11.6	7.99	13.5	10.5	17.5	13.2	7.48	7.37 18.5
			6		1	2	7	9		8
1-Hydroxy-2-b	C ₄ H ₈ O ₂	0.87	1.48	0.92	2.33		0.88	0.98		
utanone										
Acetoin	C ₄ H ₈ O ₂		1.77	1.28	3.14		2.56	1.11	0.82	1.62
2-Butanone,	C ₅ H ₁₀ O ₂				0.77					
4-hydroxy-3-m										
ethyl-										
Cyclopentano	C ₅ H ₈ O		0.81		1.33		1.00		0.53	
ne										
2,5-Hexanedio	C ₆ H ₁₀ O ₂							0.58		
ne										
Cyclopentano	C ₆ H ₁₁ O		1.20	1.50	2.85	2.82	2.70	3.59	2.55	2.44 3.65
ne, 2-methyl-										
Cyclohexanon	C ₆ H ₁₁ O ₂			0.86						
e, 2-hydroxy-										
3-Hexanone	C ₆ H ₁₂ O									1.80
4-Hydroxy-3-h	C ₆ H ₁₂ O ₂		1.70					2.05	0.66	0.91

exanone					
3-Oxabicyclo[	C ₆ H ₆ O ₃				0.76
3.2.0]heptane					
-2,4-dione, cis-					
2-Cyclopenten	C ₆ H ₈ O	1.90		1.59	1.35
-1-one,					
2-methyl-					
2-Cyclopenten	C ₆ H ₈ O	0.60		0.62	0.69
-1-one,					
3-methyl-					
1,2-Cyclopent	C ₆ H ₈ O ₂	0.82			
anedione,					
3-methyl-					
2-Cyclopenten	C ₇ H ₁₀ O	0.76	0.79	0.65	0.54
-1-one,					
2,3-dimethyl-					
2-Cyclopenten	C ₇ H ₁₀ O			0.53	
-1-one,					
3,4-dimethyl-					
1,3-Cyclohexa	C ₇ H ₁₀ O ₂		0.61	0.88	

e,						
4,4-dimethoxy						
-						
Ethanone,	C ₈ H ₁₄ O					0.51
1-cyclohexyl-						
Cyclohexane,	C ₈ H ₁₄ O ₃	0.70	1.05	0.86	0.91	1.36
1,1-dimethoxy						
-						
3-Heptanone,	C ₈ H ₁₆ O					0.74
4-methyl-						
3-Octanone	C ₈ H ₁₆ O					0.86
5-Hydroxy-4-o	C ₈ H ₁₆ O ₂		1.92			
ctanone						
6a-Methyl-hex	C ₉ H ₁₂ O ₂		0.54			
ahdropentale						
ne-1,6-dione						
1-Propanone,	C ₉ H ₁₆ O					0.56
1-cyclohexyl-						
Cyclohexane,	C ₉ H ₁₆ O				0.57	
(1-methylethyl						

idene)-

Ethanone, C₉H₈O₃ 1.08

1-(2-hydroxy-6

-methoxyphen

yl)-

2-Propanone, C₁₀H₁₂O₃ 1.53

1-(4-hydroxy-3

-methoxyphen

yl)-

3,5-Dimethyl- C₁₀H₂₀O 0.99

4-octanone

4-Decanone C₁₀H₂₀O 0.85

4-Octanone, C₁₀H₂₀O₂ 0.88 0.56

5-hydroxy-2,7-

dimethyl-

4-Methyl-3,5- C₁₁H₂₀O₂ 0.75

decandione

1,1-Di(isobutyl C₁₁H₂₂O 0.63

)acetone

3,4-O-Isopropylidene-d-galactose	C ₁₂ H ₂₀ O ₆	0.72									
4-(2,2,6-Trimethyl-7-oxabicyclo[4.1.0]hept-4-en-1-yl)pent-3-en-2-one	C ₁₄ H ₂₀ O ₂	0.60									
3-Oxaspiro[5.5]undecane-1,5-dione, 4-methyl-3-phenyl-	C ₁₇ H ₂₀ O ₃	0.57									
Ethers		5.88	5.63	6.90	7.25	5.77	8.52	2.32	3.95	4.78	4.30
Oxirane, (methoxymethyl)-	C ₄ H ₈ O ₂			1.33			1.55				0.94
Butane, 2-methoxy-	C ₅ H ₁₂ O		1.88		2.26						1.67
Ethane, C ₅ H ₁₂ O ₃				4.29							

1,1,1-trimet

hoxy-

1-Propene, $C_6H_{10}O$

0.54

1-(2-propen

yloxy)-, (Z)-

2,2-Dimetho $C_6H_{14}O_2$

0.51

1.63

1.51

0.81

0.77

1.20

xybutane

1,4:3,6-Dian $C_6H_8O_4$

0.71

hydro-.alph

a.-d-glucopy

ranose

Furan, $C_6H_{12}O_3$

2.42

tetrahydro-

2,5-dimetho

xy-

1,1-Dimetho $C_7H_{14}O_2$

1.95

1.76

1.51

0.87

0.56

0.90

0.90

xycyclopent

ane

1,3-Dioxane, $C_7H_{16}O_2$

0.62

2-ethyl-5-m

ethyl-

5H-Cyclopent	$C_8H_{12}O_2$	0.54		0.67	0.94	0.68	0.51
--------------	----------------	------	--	------	------	------	------

ta-1,4-dioxin

,

4a,6,7,7a-tetrahydro-2-

methyl-,

trans-

Apocynin	$C_9H_{10}O_3$	0.76	0.69	0.66	0.52	0.61	0.78	0.72	0.71
----------	----------------	------	------	------	------	------	------	------	------

Methyl	$C_9H_{16}O_6$						1.38
--------	----------------	--	--	--	--	--	------

3,4-ethylidene

ne- α -D

-galactopyranoside

noside

1-Butene,	$C_9H_{18}O$	0.59
-----------	--------------	------

3-butoxy-2-

methyl-

1,3-Dioxepane,	$C_9H_{20}O_2$	0.66
----------------	----------------	------

ne,

2-methyl-2-

propyl-

Methyl-(2-h $C_{10}H_{14}O_3$ 0.74 1.20 0.89 1.22 1.01 0.92 1.18 0.79

ydoxy-3-eth

oxy-benzyl)e

ther

1,4-Dimetho $C_{10}H_{16}O_2$ 0.81

xy-2,3-dimet

hylbenzene

Galactosept $C_{11}H_{22}O_6$ 0.71

anoside,

methyl

2,3,4,5-tetra

-O-methyl-, .

alpha.-D-

Benzene, $C_{14}H_{14}O_2$ 0.55

1,1'-[(1,2-di

methyl-1,2-

ethanediyl)b

is(oxymethy

lene)]bis-

hydro-

o-Cymene	$C_{10}H_{14}$		1.45	1.07	0.55
----------	----------------	--	------	------	------

Azulene	$C_{10}H_8$		0.54		0.87
---------	-------------	--	------	--	------

Naphthalen	$C_{10}H_8$	0.70	1.03		1.05
------------	-------------	------	------	--	------

e

Naphthalen	$C_{11}H_{10}$		0.54	0.60	
------------	----------------	--	------	------	--

e, 1-methyl-

Naphthalen	$C_{11}H_{10}$		0.56		0.51
------------	----------------	--	------	--	------

e, 2-methyl-

Naphthalen	$C_{12}H_{12}$			0.51	
------------	----------------	--	--	------	--

e,

1,5-dimethyl

-

Acenaphthyl	$C_{12}H_{14}$				0.64
-------------	----------------	--	--	--	------

ene,

1,2,2a,3,4,5-

hexahydro-

Naphthalen	$C_{14}H_{16}$			0.53	
------------	----------------	--	--	------	--

e,

1-methyl-7-(

1-methyleth

yl)-

Neoisolongif C₁₅H₂₂

0.67

olene,

8,9-dehydro

-

2H-2,4a-Met C₁₅H₂₄

0.61

hanonaphth

alene,

1,3,4,5,6,7-h

exahydro-1,

1,5,5-tetram

ethyl-, (2S)-

2,4,4,6-Tetr C₁₇H₂₈

0.92

amethyl-6-p

henylheptan

e

Retene C₁₈H₁₈

0.68

1-Methyl-10 C₁₉H₂₈

0.57

,18-bisnorab

ieta-8,11,13

-triene

Naphthalen $C_{19}H_{28}$

1.55 1.37

e,

6-ethyl-1,2,

3,4-tetrahyd

ro-1,1,4,4-te

tramethyl-7-

(1-methylet

henyl)-

18-Norabiet $C_{19}H_{34}$

1.96

ane

352

353

354

355

356

357

358

359

360

361 **Table 4** The analysis of gas obtained by different treatments

	Case	Case	Case	Case	Case	Case	Case	Case	Case
	1	2	3	4	5	6	7	8	9
Initial (MPa)	1.38	2.76	4.14	1.38	2.76	4.14	1.38	2.76	4.14
Final (MPa)	1.10	2.28	2.83	0.90	2.21	2.83	0.62	1.38	2.28
Maximum (MPa)	4.34	6.27	7.24	710	4.90	8.41	5.10	6.90	8.96
H ₂ (Volume %)	62.36	64.36	83.44	49.85	70.60	87.82	51.59	84.53	57.08
CO ₂ (Volume %)	32.83	32.72	14.99	33.34	23.87	11.34	33.17	0.00	32.86
CO (Volume %)	2.68	2.54	1.35	14.22	5.05	0.57	11.67	0.00	7.38
CH ₄ (Volume %)	0.86	0.11	0.11	1.09	0.19	0.06	1.91	4.74	1.06
C ₂ H ₄ (Volume %)	0.09	0.18	0.00	0.02	0.03	0.04	0.01	2.89	0.85
C ₂ H ₆ (Volume %)	0.63	0.06	0.06	1.00	0.13	0.02	1.52	5.71	0.69
C ₃ H ₆ (Volume %)	0.00	0.03	0.00	0.14	0.01	0.00	0.12	0.20	0.08
C ₃ H ₈ (Volume %)	0.54	0.00	0.05	0.34	0.12	0.00	0.00	1.93	0.00
C ₄ H ₈ (Volume %)	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.00	0.00
C ₄ H ₁₀ (Volume %)	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.00	0.00

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