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CATALYTIC HYDROLIQUEFACTION OF SPRUCE WOOD
- ELEMENTAL BALANCE AND EFFECT OF CATALYST -

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ABSTRACT

Catalytic hydroliquefaction of spruce wood particles (ca. 3 mm), suspended in a process derived slurry oil, has been conducted in a three 1-liter-capacity autoclave system using palladium on active charcoal in concentrations of 1 %, 0.5 % and 0.1 % (based on wood) and red mud (10 %) as a once-through catalyst. In a series of successive experiments the carrier slurry oil was separated from the net product oil (NPO) by trapping in a hot separator in order to recycle it. Decreasing Pd amounts increased viscosities of the carrier. In the presence of Pd, wood conversion rates of 95-97 % were obtained and yields of light- and middle distillate NPO decreased from 34 to 30 % when the amount of catalyst was reduced. The use of red mud gave NPO yields of 20 % and char yield increased to 37-43 %. In experiments with Pd, 4 % hydrogen and with red mud 1.7 % hydrogen (based on wood) was consumed.

The NPO's were characterized by determination of asphaltene content, molecular weight distribution, elemental composition and boiling point distribution. In all experiments, the oils obtained with Pd had superior properties to those described in the literature and obtained in runs with red mud. Exemplary gas analyses were carried out to close the material balance. The distribution of carbon, hydrogen and oxygen in the liquefaction products was determined and elemental mass balances of some experiments are presented.

INTRODUCTION

The conversion of renewable lignocellulosic materials into liquid products has been investigated for many years. These R and D activities were induced by the dramatic increase of fossil energy prices. A promising conversion route is direct liquefaction which aims at maximizing oil yields. Inevitably, gas, water, water-soluble products and small amounts of solid residues are also produced during this type of reaction. Due to decreasing oil prices and the relatively slow progress in thermal biomass conversion processes the R and D activities are still carried out in laboratory equipment and bench-scale units. But though curtailed, that work still proceeds.

The optimum temperature range for direct wood liquefaction is now considered to be between 300 and 400°C, but investigations are going on to find the most suitable catalyst. Investigations on the reaction time and pressure, which have also interrelations with catalyst and process temperature are also ongoing.¹⁻⁵

In the beginning of thermochemical biomass liquefaction, water-soluble inorganic catalysts were mainly used to convert lignocellulosic particles, suspended in water, to an oil in the presence of carbon monoxide.⁶⁻⁹ The oils obtained were very viscous and difficult to separate from the water phase. They had a high oxygen content in the range of 20 %. Another disadvantage of this process was the high steam pressure at reaction tempera-

tures of about 350°C.¹⁰ Further information about different approaches for biomass liquefaction can be found elsewhere.^{11,12} Recently, solubilization of poplar wood using only steam without catalyst was achieved.¹³ The product was totally soluble in acetone and suitable for further hydroprocessing.

In our earlier experiments^{14,15} attention was focused on catalytic hydrogenation using a heterogeneous catalyst like palladium on active charcoal and to a minor extent using red mud, which is an inexpensive once-through catalyst. Because of the expensive Pd catalyst which must be recycled and reactivated, the disposable catalyst red mud was included into the studies. Red mud is obtained as a by-product of the aluminium producing industry and contains iron in the form of Fe_2O_3 as the active hydrogenation component. The behaviour of different lignocellulose was studied systematically. Wood was suspended in water and hydrogen pressures reached up to 30 MPa. Highest oil yields were obtained from organosolv lignins (ca. 62 %), lower yields from cellulose (29.3 %) and lowest yields from bark (20.7 %). Wood yielded between 40 and 46 % of an oil. A serious disadvantage of these experiments was that the oxygen content of the oils was high (20 to 27 %).

These results prompted a study of a slurry oil hydroliquefaction process using a high boiling wood tar and palladium on active charcoal as catalyst. An autoclave system of three 1-liter capacity batch autoclaves was used for the hydroliquefaction (see

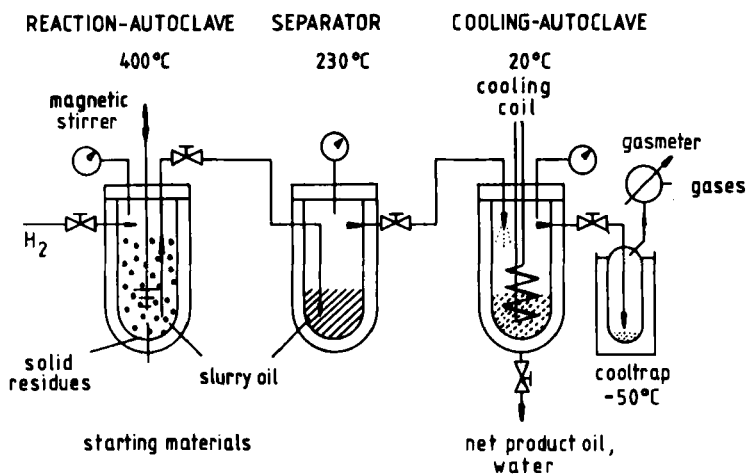


FIGURE 1. Autoclave system for wood liquefaction.

Figure 1). In the course of the successive experiments the high boiling oil fraction was separated after each run and reused for the next one.⁵

This paper describes the continuation of our hydroliquefaction experiments. The effects of the amount of palladium and red mud as well as variations of the wood/palladium ratios were studied. Careful analyses of the liquefaction products were made in an effort to ensure closing the elemental mass balance.

EXPERIMENTAL

Liquefaction Procedure

The reactor system is depicted in Figure 1 and consists of three 1-liter-capacity autoclaves.

The following procedure is typical for a hydroliquefaction experiment: 100 g (dry basis) of ground pine wood (particle size 3 mm) were thoroughly mixed with 50 g wood tar together with the corresponding catalyst (1-10 g Pd on active charcoal or 10 g red mud). The reactor was then charged with the prepared biomass. After sealing, the reactor was flushed twice with hydrogen and then pressurized with hydrogen to 10 MPa. The gas volume was additionally measured with a commercial gas meter. The reaction temperature of 380°C was reached within 60 min and held for 15 min. Then the reaction was interrupted by opening a valve between the reactor and the hot separator. The products in the gas phase passed through a heated line into the hot separator, whose temperature was maintained at 230°C. Here, the high boiling carrier condensed and the remaining products in the gas phase were passed through another heated line into a water-cooled condenser. Any residual condensable products were trapped in cooler held at -50°C. The final gas volume was also measured with the gas meter and an aliquot of the gas was stored in a gastight bag.

Separation of products

Two liquid phases are obtained from the 20°C cooling receiver: water and the net product oil (NPO) which has a density of 0.92 g/mL. Separation of water and NPO was done in a separatory funnel. After separation the water was extracted with methylene chloride and weighed. The main portion of the catalyst and char

remained in the reaction autoclave and was removed. The autoclave system was washed with methylene chloride, this wash combined with the high boiling carrier oil coming from the hot separator and the mixture filtered to collect small amounts of catalyst and solids. All solids collected were extracted overnight with methylene chloride, dried and weighed. Fractions of methylene chloride containing the organic extracts were combined, dried over sodium sulfate, evaporated and the organic oil residue was then added to the carrier. Small amounts of low boiling compounds from the final cooler were combined with the NPO which was then weighed.

Catalysts

Palladium on active charcoal (10 % Pd loading) type E 10 R/D was obtained from DEGUSSA, Frankfurt. Red mud was delivered by Bergbauforschung, Essen, with a content of 30.8 % Fe_2O_3 and 22.7 % Al_2O_3 .

Carrier oil

The carrier oil for the start-up of the experiments was obtained from Commentz & Co., Hamburg. It consisted of softwood tar from the charcoal production in Scandinavia and contains unknown amounts of tall oil pitch. The following analytical data were given by the company: viscosity at 20°C 710 cP, acid number

65, saponification number 110, solubility in benzene 99 %, water 0.9 %, ash 0.2 %.

Analysis of the Net Product Oil (NPO)

Asphaltene content was determined as follows: 1 mL of the NPO was added to 10 mL n-hexane and centrifuged. The supernatant solution was rejected and the precipitate washed with n-hexane, centrifuged again, dried and weighed.

Simulated distillation was employed according to ASTM D 2887-73.

Elemental composition was determined on a Carlo Erba 1104 elemental analyzer. The heating values were calculated according to Dulong's formula (see 5).

Molecular weight distribution was determined by High Performance Gel Permeation Chromatography using a column (600 x 7.7 mm, PL-laboratories, England) packed with poly(styrene-divinylbenzene) spherical particles of 10 μm size and 50 A pore size. The solvent employed was doubly distilled methylene chloride. Details on the calibration procedure can be found elsewhere.¹⁵

Analysis of the Product Gases

Gas chromatographic determination of the C1-C4 hydrocarbons was performed on a Perkin Elmer Sigma 2 apparatus. Separation was on a fused silica capillary PLOT-column (50m x 0.32mm, CHROMPACK, Netherlands) coated with aluminium oxide. Detection was with a

FID and the oven temperature was held for 10 min at 100°C, then raised at 40°C/min to 200°C. Quantification was accomplished using commercial gas mixtures as reference standards. These were injected several times using different volumes, so that individual calibration curves of all light hydrocarbons could be obtained.

Carbon monoxide and carbondioxide were quantified with an ORSAT apparatus. The volumes of hydrocarbons and oxygen containing gases were subtracted from the residual total gas volume to give an estimate of the residual hydrogen (see Table 2).

RESULTS AND DISCUSSION

Yields on Liquefaction Products

Considering the reproducibility of the yields reported in Table 1 one should be aware of the experimental procedures, which were used to collect quantitatively the gases, liquids and solid products from the three 1-liter capacity autoclave system. The run numbers represent those done in the order presented to demonstrate clearly the reproducibility and the development of product yields. No explanation can be given for the consistent decrease in total oil for the 1 % Pd runs and the consistent increase in total oil for the 0.5 % Pd runs.

Table 1 presents the yields of all liquefaction products and the properties of the net product oils (NPO), which is the most

TABLE 1
Yields and Analytical Data of Hydroliquefaction Products from Spruce Wood with Palladium and Red Mud as Catalyst.

CATALYST*	1% Pd			0.5% Pd			0.1% Pd			10% RED MUD								
	7	8	10	12	13	14	15	16	17	18	19	20	21					
RUN No.	380	380	380	380	380	380	380	380	380	380	380	300	300					
TEMP. (°C)	380	380	380	380	380	380	380	380	380	380	380	300	300					
NPO (g)	33.3	38.1	33.2	32.1	34.2	25.5	30.1	29.9	29.4	28.7	29.5	36.3	24.1	30.0	19.9	9.3	12.0	10.6
CARRIER *	54.5	46.8	50.2	48.8	50.1	53.8	51.7	54.1	56.9	54.1	45.1	56.6	61.6	54.4	25.7	50.0	49.2	49.6
Σ OIL *	87.8	84.9	83.4	80.9	84.3	79.3	81.8	84.0	86.3	82.8	74.6	92.9	85.9	84.4	45.6	59.3	61.2	60.2
SOLIDS *	7.6	10.6	9.6	10.5	9.6	15.3	10.2	9.8	8.9	11.1	-	5.5	9.6	7.6	43.3	38.7	37.3	38.0
WATER *	31.0	31.1	31.0	30.6	31.0	27.4	25.0	26.9	29.5	27.2	25.9	26.3	25.6	25.9	22.2	21.1	19.8	20.4
CO ₂ *	6.9	9.4	7.7	10.0	8.5	11.0	12.4	15.5	11.2	12.5	8.6	9.6	9.2	9.1	20.4	17.5	17.1	17.3
CO *	3.1	3.2	3.0	3.8	3.3	4.0	5.4	4.3	4.1	4.5	3.1	3.2	1.7	2.7	2.4	1.2	3.8	2.5
CH ₄ *						8.0		6.4			4.3				6.2			
C ₂ H ₆ *						5.1		4.2			2.6				4.1			
C ₃ H ₈ *						5.1		4.4			2.8				3.5			
C ₄ H ₁₀ *						2.0		1.7			1.1				1.3			
Σ GAS *						35.2		32.0			23.6				37.9			
ASPHAL- TENES	(%) 1.1	1.2	0.4	0.8	0.9	3.3	4.6	8.0	4.1	5.0	7.1	6.3	7.3	6.9	1.9	1.8	4.4	3.1
SIM. DIST. BP< 220°C	(%) 47	42	50	48	47	45	43	40	43	44	33	28	35	32	30	21	27	24
220-360°C	53	57	50	52	53	55	47	60	57	56	67	69	61	65	67	72	65	68
BP> 360°C	0	1	0	0	0	0	0	0	0	0	0	3	4	3	3	7	8	8
C	(%) 77.4	78.1	79.6	78.1	78.4	75.0	73.8	77.4	76.8	75.8	81.2	78.9	77.1	79.1	79.7	70.4	77.9	74.2
H	10.4	10.6	10.7	10.4	10.5	9.5	10.0	10.2	9.9	9.9	11.2	9.9	9.6	10.2	9.7	8.8	9.8	9.3
O*	11.7	11.3	9.7	11.5	11.1	15.5	16.2	12.4	13.3	14.3	7.6	11.2	13.3	10.7	10.6	20.8	12.3	16.6
HV* MJ/kg	39.2	39.7	40.6	39.3	39.7	36.3	36.5	38.7	37.9	37.4	42.3	38.9	37.5	39.6	39.0	32.7	38.3	35.5
M _w (Dalton)	123	121	114	121	121	129	124	123	123	125	124	123	122	123	122	126	126	126

* by difference, % CATALYST based on dry wood, all other % data based on net product oil (NPO); * according to Dulong⁵

important fraction of the liquefaction procedure. NPO yields were highest with 1 % Pd (runs 7-10). The reproducibility was the best within this set of experiments. The low- and middle-distillate fractions amount on an average to 34 %. Initially, 50 g of carrier oil were used for the preparation of the wood-oil-slurry. As can be seen from Table 1, the average carrier oil yield of these experiments is about 50 g demonstrating its complete recovery. This fact is an important prerequisite for a continuous operation of the process. The carrier oils of these runs were syrups at room temperature.

The yield of NPO decreases slightly, when 0.5 % Pd is used. On an average it amounts to 29 %. On the other hand, the yield of carrier oil increases to 54.1 % in these experiments indicating a lower degree of hydrogenation in comparison with runs 7 - 10. Possibly, radicals formed by the thermal cleavage are not effectively stabilized with hydrogen by the small amounts of catalyst. Hence, recombination reactions are possible leading to higher molecular weight products with a higher boiling point. As a consequence the viscosity of the carrier increased also essentially.

When 0.1 % Pd is used the average yields of NPO do not differ much from the results discussed before, but the reproducibility is less satisfactory. This can be explained by an irregular distribution of such a small amount of catalyst in the wood-oil-slurry. The viscosities of the carrier oils are even

higher than those from run 12 to 15. These oils were only fluid at $\geq 60^{\circ}\text{C}$.

The use of red mud resulted in a significant decrease of the NPO yields. Only 20 % NPO is obtained at 380°C and 11 % at 300°C . According to these results red mud is unsuitable for that kind of hydroliquefaction process. This statement becomes even more evident, when the yields on solid residues are compared. Char yields with red mud as catalyst are in the range of 37 to 43 %, whereas the amounts of solid residues in the experiments with Pd are between 6 and 15 %.

Oxygen removal from lignocellulosic biomass is an essential step in hydroliquefaction and is effected by its removal in the form of CO_2 , CO and water. The last product is favoured if palladium is used. In this case the amount of the water fraction varies between 25 and 31 %. Red mud yields only 20 to 23 % water but the CO_2 yield amounts to 20 wt % at 380°C . Under the same conditions the average CO_2 production in runs with Pd is only 10 wt %.

The amount of Pd influences the yield and composition of C1-C4 hydrocarbons (HC). According to Table 1, 11 wt % HC were obtained with 0.1 % Pd and with 0.5 % Pd the HC yield amounts to 20 wt %. Complete gas analyses were performed with runs 12, 15, 17 and 19 in order to close the elemental mass balance. The gaseous hydrocarbons of runs 7 to 10 could not be analyzed for experimental reasons.

TABLE 2

Determination of the Hydrogen Consumption.

CATALYST		0.5% Pd		0.1% Pd		RED
						MUD
RUN No.		12	15	17	19	
H ₂ before reaction	I	90.3	91.2	89.0	87.5	
total GAS after						
reaction	II	71.4	70.8	62.1	95.3	
PRODUCT GAS after						
reaction	III	27.2	23.9	17.2	26.4	
II - III=residual H ₂	IV	44.2	46.9	44.9	68.9	
I - IV =consumed H ₂	V	46.1	44.3	44.1	18.6	
% H ₂ consumed (b.o. wood)		4.1	4.0	3.9	1.7	
		=(V+2) ÷ 22.4				

(data from lines I-V in liters)

With the data obtained from the quantitative gas analysis the hydrogen consumption was calculated (see Table 2). A consumption of 4 % hydrogen, based on wood, is observed in runs with Pd. This value corresponds to about half of the hydrogen present before the reaction. The consumption of 4 % hydrogen represents a value in a realistic range, e.g. in the German Kohleöl-Process about 6 % H₂ is consumed. The poor hydrogenation power of red mud is again demonstrated as this catalyst effected the consumption of only 1.7 % H₂. The increased hydrogen consumption in experiments with Pd may be related to the increased water formation.

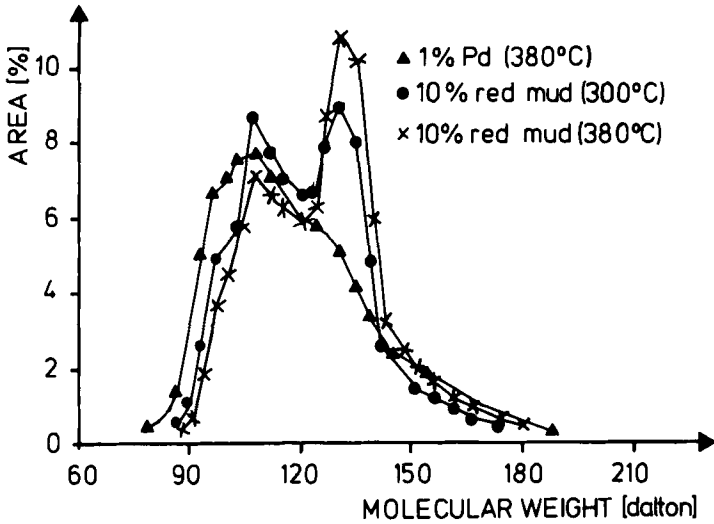


FIGURE 2. Pressure-time-plot of liquefaction experiments with spruce wood using Pd and red mud as catalyst.

The gas volume after hydroliquefaction with red mud is always larger than the initial hydrogen volume. Low hydrogen consumption, low water formation, low NPO yield and high yields of solid residue can be explained by an insufficient catalytic effect of red mud towards hydrogenation. In Figure 2, pressure in the reactor is plotted against time to show the course of the hydrogenation reaction. During the first 25 min the pressure rises slowly. After that time thermal degradation starts, followed by subsequent hydrogenation. The slope of the curves depends on the kind and amount of catalyst. The more efficient the hydrogenation the slower the pressure increase. According to Figure 2, and in agreement with other analytical data, hydrogenation

tion efficiency increases in the following order: red mud <0.1 % Pd <0.5 % Pd <1.0 % Pd.

Net Product Oil Characterization

Some important oil characteristics are presented in Table 1. The asphaltene content rises from 1 to 7 % with decreasing Pd amounts. The asphaltene contents of the NPO's with red mud vary between 2 and 3 %. It is remarkable that the solubility of the NPO's in n-hexane is extremely good taking into account that biomass derived oils from other processes described in the literature¹⁷ are rather polar and only soluble in acetone, diethyl-ether, dichloromethane or toluene. The low asphaltene content can be explained by the relatively low oxygen content the low average molecular weight (see Table 1).

Results of simulated distillation reveal that oils obtained with 0.1 % Pd and red mud contain portions of 3 to 11 % with a high boiling temperature >360°C. The light-distillate fraction with a boiling point <220°C is largest with 1 % Pd and amounts up to 50 % of the NPO. Typical boiling point distribution curves of NPO's from liquefaction experiments with 1 % and 0.1 % Pd and 10 % red mud are depicted in Figure 3.

From the curves it can be deduced that a charge of 1 % Pd gives the best results indicating that the hydrogenation efficiency strongly influences the boiling characteristics of the oils.

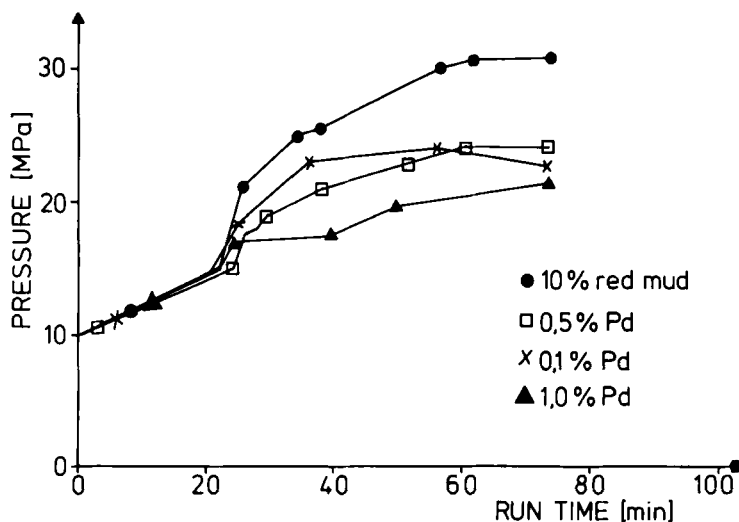


FIGURE 3. Boiling point distribution curves of net product oils from liquefaction of spruce wood obtained with Pd and red mud as catalyst.

The energy content of the oils produced by hydroliquefaction plays an important role in the utilization as a fuel. Table 1 shows calculated heating values based on elemental analyses. The average heating value of the Pd runs is about 39.6 MJ/kg and the energy content of the red mud runs is in the range of 35.5 to 39 MJ/kg. In comparison to the heating value of wood (18 MJ/kg), a twofold increase of the energy content is achieved.

The average molecular weights (\bar{M}_w) of the NPO's, which are presented in Table 1 do not show significant differences. However, distinctive changes can be observed by comparing the standardized molecular weight distribution curves, as displayed in Figure 4.

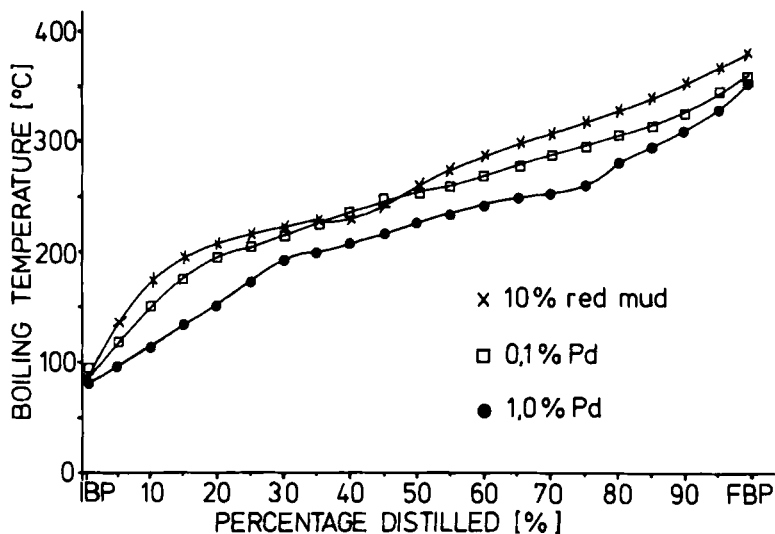


FIGURE 4. Standardized mol weight curves of net product oils from liquefaction of spruce wood with Pd and red mud as catalyst.

The bimodal distribution curves from the runs with red mud are very characteristic, indicating a less advanced degradation in comparison with Pd as catalyst. The mol weight distribution curve from Pd shows in the region of 135 daltons only a small shoulder and its maximum is at 110 daltons. The red mud runs yield more products with higher molecular weights of about 135 daltons. Surprisingly high is the amount of larger molecules at elevated reaction temperatures (see runs with red mud at 300 and 380°C). At higher temperatures recombination reactions occur which is reflected by the distinct peak of the mol weight distribution curve of the run with red mud at 380°C.

TABLE 3

Elemental Mass Balance of Liquid and Gaseous Products Obtained from Liquefaction of Spruce Wood

RUN No.	CARBON (g)			HYDROGEN (g)			OXYGEN* (g)		
	15	17	19	15	17	19	15	17	19
<u>ORIGIN:</u>									
WOOD	50.0	50.0	50.0	6.0	6.0	6.5	44.0	44.0	44.0
CARRIER	41.0	41.4	43.2	4.0	4.4	4.4	5.1	4.2	2.4
HYDROGEN				7.6	7.4	7.3			
Σ	91.7	91.4	93.2	17.6	17.8	17.7	49.1	48.2	46.4
<u>distributed in:</u>									
NPO	22.6	28.6	15.6	2.9	3.6	1.9	3.9	4.1	2.1
CARRIER	46.3	45.0	22.5	4.3	4.1	2.1	6.3	7.5	1.1
GASES	19.5	12.5	18.5	3.5	2.3	3.1	11.7	9.7	16.5
WATER	1.1	1.1	0.6	3.3	2.9	2.2	26.2	23.4	17.6
RESIDUAL H ₂				3.7	3.6	5.6			
Σ	89.5	87.2	66.2	17.7	16.5	14.9	48.1	44.7	37.4
RECOVERY(%)	97.6	95.4	71.0	100.0	92.7	84.2	98.0	92.7	80.6
*by difference									

Elemental Mass Balance

Based on the results of the quantitative determination of all reaction products an elemental mass balance of liquid and gaseous products was established (Table 3). Overall recoveries of carbon, hydrogen and oxygen are between 92.7 and 100 % in runs with Pd. These values are essentially higher than the corresponding recoveries for the run with red mud (71.0 to 84.2 %). This

can be explained by the high amount of solid residue which is not included in the elemental balance.

The carbon content of wood and carrier is about 92 g before the reaction. With Pd as catalyst 75-80 % of the initial carbon content is present in the NPO and carrier oil, 13-21 % can be detected in the product gases and a very small amount of about 1.2 % remains in the water phase.

Hydrogen distribution is also more favourable in the runs with Pd as the oils have 35 to 90 % higher hydrogen contents than the oil from experiments with red mud.

About 50 % of the oxygen from the biomass is converted into water when Pd is used as catalyst. Approximately 25 % of the original oxygen can be found in the gas and 25 % in the oil phase. With red mud only 38 % of the biomass oxygen is converted to water and 35 % is detected as oxygen containing gases. Only 6 % is in the oil phase and the rest remains in the solid residue.

CONCLUSIONS

Wood can be converted to an n-hexane soluble oil in a yield of approx. 35 wt % by direct catalytic hydroliquefaction in the presence of palladium as catalyst. From the results it can be concluded that the use of 1 % Pd gives higher oil yields and better product qualities than the use of 0.5 or 0.1 % Pd. The differences are not very significant, so that the use of lower catalyst

amounts can be recommended, especially with reference to costs of catalyst and recovery. Red mud, although successfully used in the German coal conversion technology, is unsuitable for wood liquefaction. This catalyst probably needs higher temperatures to obtain an optimum hydrogenation efficiency. This requirement cannot be fulfilled in wood liquefaction as it leads to increased char and gas formation.

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