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## HYDROGENATION OF OIL PRODUCED BY NAPHTHA STEAM PYROLYSIS – DETERMINATION OF CATALYST ACTIVITY

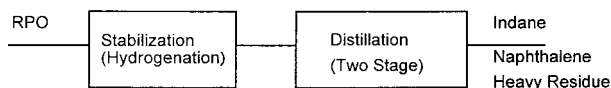
*Residual pyrolysis oil (RPO) produced as a by-product of naphtha steam pyrolysis was hydrogenated (160–280°C; 60 bar; trickle-bed reactor with Co–Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) with the aim of suppressing the polymerization of the unsaturated compounds present in the oil (styrene, (–methylstyrene, 4-, 5- and 6- methyl–indene and others) which give a highly aromatic resin. The influence of temperature on the rate of hydrogenation was investigated at a constant liquid space velocity (LHSV) of 1 h<sup>-1</sup> and hydrogen/oil ratio of 600 Nm<sup>3</sup>/m<sup>3</sup>, while the influence of liquid space velocity (1– 3 h<sup>-1</sup>) was analyzed at 200°C and 60 bar at the same hydrogen/oil ratio. GC and GC–MS analysis of the hydrogenated oil were carried out on the hydrogenated sample, as well as viscosity measurements, which showed that no polymerization occurred in the case of stabilized (hydrogenated) oil. The optimal hydrogenation temperature and LHSV values were 220°C and 1h<sup>-1</sup>, respectively. The result of the longterm hydrogenation test was used to study the kinetics of the catalyst deactivation process by determining the rate constants in the case of indene, 4-methyl–indene and 5- and 6-methyl–indene hydrogenation. Using the obtained rate constants, the conversion of the above compounds was mathematically simulated showing satisfactory agreement with the experimentally obtained values.*

The physical characteristics of residual pyrolysis oil (RPO) are given elsewhere [1]. RPO can be used as a fuel, however better economical valorization can be realized by:

- the production of special chemicals, e.g. naphthalene;
- polymer swelling;
- wood protection;
- insecticide production;
- the preparation of coating materials;
- the production of highly aromatic lighter oil;
- the production of aromatic resins;
- coke production;
- the production of special additives for making industrial bitumen.

This work involves the analysis of RPO stabilization by hydrogenation with the goal of suppressing polymerization of the unsaturated compounds which are present in the oil (styrene, (–methylstyrene, 4-, 5- and 6-methyl–indene and others).

Hydrogenation leads to the formation of saturated double bonds in styrene and indene type compounds, but also under severe hydrogenation conditions to the unfavorable hydrogenation of aromatic compounds (naphthalene). The production of naphthalene and indane can be realized according to the following technological route:



The influence of temperature and the LHSV on the rate of hydrogenation was investigated under a constant pressure of 60 bar and a hydrogen to oil ratio of 600 Nm<sup>3</sup>/m<sup>3</sup>. The experiments were performed at 160, 200,

240 and 280°C with a LHSV of 1h<sup>-1</sup>, and at 200°C with a LHSV of 1, 1.5 and 3 h<sup>-1</sup>. To study the behaviour of the catalyst during hydrogenation, a longterm hydrogenation test was performed which lasted 120h. During this experiment the temperature changed from 200 to 220°C. The conversion of indene, 4-methyl–indene and 5- and 6-methyl–indene, determined by GC analysis, was used to calculate the kinetic parameters of hydrogenation, as well as of catalyst deactivation and reactivation [2]. The kinetic data were used to perform a mathematical simulation of the so-called longterm deactivation test. GC analysis of the hydrogenation products was also used to follow the possible hydrogenation of the aromatic rings. The viscosity of the RPO was measured to see whether polymerization took place during the hydrogenation.

### EXPERIMENTAL

The hydrogenation of RPO was performed in a trickle-bed reactor (5.8 cm i.d. and 520 cm length pipe), where 35 g of the catalyst (50 cm<sup>3</sup>) were diluted by using inactive alumina in the volumetric ratio 1:2 (catalyst:alumina). On both sides of the catalyst bed, a guard bed of inert alumina, 0.5 cm (below) and 1 cm (above the bed), was installed. A thermowell (2.2 cm i.d.) was placed in the center of the catalyst bed allowing precise catalyst temperature measurement during hydrogenation. The commercial catalyst (BASF M8–14, extrudate 1.3 mm) was sulfidized *in-situ* using the RPO with CS<sub>2</sub> (22.5 gCS<sub>2</sub>/1000 cm<sup>3</sup> of residual oil, i.e. 2.2 % S in the oil) at 40 bar and 300°C (maximum), using the standard heating rate of 30–50 °/h.

When experimental conditions were attained (pressure, temperature and flow rate of RPO), hydrogenation was carried out for at least 2–3 hours, when steady state conditions were established. The liquid product of the hydrotreated RPO was collected in regular time intervals (30 min) for detailed GC analysis.

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### Influence of temperature

The influence of temperature was analyzed at the beginning of hydrogenation when the catalyst showed its initial and highest activity. The experimental conditions were: 60 bar, LHSV=1 h<sup>-1</sup> (RPO=50 cm<sup>3</sup>/h and H<sub>2</sub>=30 dm<sup>3</sup>/h). The hydrogenation was first analyzed at 160°C, and then, when the desired quantity of the hydrotreated product was collected, the hydrogenation temperature was raised to 200°C. This experimental procedure was repeated at 240 and 280°C.

The results of GC analysis indicated that the quality of hydrogenated RPO at 200°C has all the desired qualities (small quantity of unsaturated compounds, oil viscosity); however, hydrogenation performed at a higher temperature (>240°C) indicated some undesirable effects in the quality of the hydrogenated products such as large decreases of oil viscosity and the saturation of aromatic compounds (e.g. naphthalene). These results undoubtedly showed that the best effects of hydrogenation could be expected at 200–220°C.

### Influence of LHSV

During RPO hydrogenation the following liquid hourly space velocities were analyzed: 1; 1.5 and 3h<sup>-1</sup>, always keeping the same hydrogen/oil ratio at the inlet of the reactor (H<sub>2</sub>/oil=600 Ncm<sup>3</sup>/cm<sup>3</sup>), as well as pressure (60 bar) and temperature (200°C). The obtained results showed that LHSV=1h<sup>-1</sup> gave the best results compared to other investigated liquid flow rates. Thus, all the investigations of the influence of temperature and LHSV on hydrogenation showed that the best results could be obtained if hydrotreatment were performed at 200–220°C, under 60 bar, LHSV=1h<sup>-1</sup> and H<sub>2</sub>/oil = 600 Ncm<sup>3</sup>/cm<sup>3</sup>.

### Analysis of catalyst activity during 120 h (longterm test) reactor steady state operation

The longterm hydrogenation test was performed as follows. *In-situ* resulfidization of the catalyst was performed after study of the influences of temperature and LHSV was completed. The same procedure was applied for resulfidization as for the fresh catalyst. The first 40 hours of longterm hydrogenation were performed at 200°C, and then, to compensate for a small drop in the catalyst activity, the temperature in the reactor was increased to 210°C, and after an additional 5 hours of hydrogenation to 220°C. Namely, analysis of hydrogenation product indicated, that to obtain a product of constant quality, this hydrogenation temperature increase was necessary to suppress the negative influence of catalyst deactivation. The hydrogenation process was quite stable during the entire 120 h of operation, with minor changes of less than 3% in the key operating parameters (pressure 60 ±0.5 bar; temperature fluctuation 0.88% at 200°C and 0.97% at 220°C; LHSV=1–1.03 h<sup>-1</sup>; hydrogen flow rate 29–31 Ndm<sup>3</sup>/h). Changes in the hydrogen flow rate were observed only when liquid product was withdrawn from

the high pressure separator. However, such disturbances lasted only 1–2 min.

### GC analysis of hydrogenation products

The liquid samples as well as samples of the gas phase collected during the hydrotreatment tests were continuously analyzed enabling complete monitoring of the hydrogenation process.

The liquid samples were analysed by capillary gas chromatography using a Varian 3400 instrument equipped with a FID detector and a Spectra-Physics System I computing integrator on a DB-5, 30 m glass capillary column with temperature programmed at 4°C/min from 60–300°C. Nitrogen was used as the carrier gas.

The gas analysis was always performed at the start of a test and then after 5 hours of operation, and always when the liquid samples were withdrawn from the high pressure separator. A Shimadzu GC (model GC-9A) instrument equipped with FID and TCD was used for the gas analysis. The following columns and detectors were used for the detection of different gases and vapours: hydrogen, molecular sieve 5A (2m), TCD at 150°C, 50 mA; hydrocarbons, 20% squalene on Chromosorb PAW (4m), FID at 150°C. Gas analysis was performed *on-line* and the main constituents of the gas phase were hydrogen (more than 99%), but also smaller quantities of C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, n-C<sub>4</sub> and i-C<sub>4</sub> were detected (less than 1%).

The results of GC analysis of the gas phase during the hydrogenation of RPO are given in Table 1. The

Table 1. GC analysis of the gas phase collected during the analysis of RPO hydrogenation at different temperatures and LHSVs

		CH <sub>4</sub> %vol.	C <sub>2</sub> H <sub>6</sub> %vol.
HYDROGENATION TEMPERATURE, °C	160	0.100	0.003
	200	0.063	0.002
	240	0.049	0.001
	280	0.010	0.004
LHSV at 200°C, h <sup>-1</sup>	1	0.063	0.002
	1.5	0.015	0.003
	3	0.005	0.002
LONG-TERM HYDRO- GENERATION (120 h) TEST TIME, h (TEMPERATURE, °C)	13 (200)	0.026	0.001
	40 (200)	0.001	0.001
	5 (210)	0.001	0.001
	24 (220)	0.001	0.003
	38 (220)	0.001	0.003

hydrogenation products were collected during the analysis of temperature and LHSV effects, and the results of GC-analysis of the liquid samples collected during these tests are presented in Table 2.

The viscosity of the liquid samples was determined at 20°C using a Vogel-Ossag viscosimeter.

## RESULTS AND DISCUSSION

GC analysis of the gas phase showed the presence of small quantities of methane, ethane, propane, butane and isobutane, in addition to hydrogen, the content of which always amounted to over 99.7% vol. and mostly to over 99.9% vol. Methane and ethane are products of the hydrodealkylation of the methyl and ethyl, i.e. vinyl (via hydrogenation) substituted components of the RPO. The change of the content of methane and ethane in the gas phase depends on the hydrogenation temperature, LHSV and catalyst activity during the longterm hydrogenation test, as shown in Table 1. The quantity of methane decreases with increasing temperature. It is difficult to give a reasonable explanation for this phenomenon. The growth of the quantity of methane in the gas phase with increase of the residence time of the oil in the reactor, i.e. with decrease of LHSV value, is understandable, as there is more time for the hydrodealkylation to take place. During the stabilization period, which proceeds to the steady state, the methane content decreases to a constant value (0.001% in this particular case). The content of ethane, however, varied irregularly. As ethane present both, a product of the hydrodealkylation of an

ethyl group, as well as of a vinyl group (via the hydrogenation of ethylene), and a vinyl group can polymerize and be regenerated through depolymerization, this irregularity could be understandable and could be caused by every disturbance of the process, for instance by taking samples from the liquid high pressure separator.

The results of GC analysis of the liquid products of RPO hydrogenation obtained during the study of the effects of temperature and LHSV are given in Table 2. Our experience showed that the total area percent values in Table 2, as well as in Table 3 should be multiplied by 0.65, to be converted to the appropriate weight percent. The results in Table 2 show that the temperature of 160°C was too low for the hydrogenation of double bonds to take place, i.e. the quantities of styrene, indene, 4-methyl-indene and 5- and 6-methyl-indene in the hydrogenated products practically did not change compared to their content in the original RPO. Increase of the viscosity from 15.8 to 20.0 mm<sup>2</sup>/s indicates, however, that polymerization took place to some extent, under that reaction condition. Hydrogenation at 200°C was very successful, as only traces of compounds with double bonds remained, the extent of polymerization (viscosity 19.6 mm<sup>2</sup>/s) was not greater than that at 160°C and no hydrogenation of the aromatic rings took place. Hydrogenation at 240°C was practically completed without hydrogenation of the aromatic rings and undesired polymerization did not take place or was compensated by desired

Table 2. GC analysis of the liquid products collected during hydrogenation tests of RPO















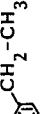
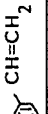

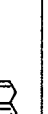
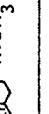




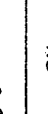
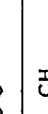
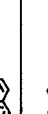
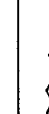

SAMPLE NUMBER	TEMPERATURE, °C	LHSV, h <sup>-1</sup>	VISCOSITY AT 20°C mm <sup>2</sup> /s	COMPONENTS WITH GC RETENTION TIMES IN SECONDS, TOTAL AREA %													
				 269	 305	 526	 537	 733	 747	 752	 757	 771	 809	 1038	 1068	 575	 657
RPO			15.8	-	0.1	0.8	2.2	0.6	2.6	-	4.7	2.6	32.5	8.8	6.1	0.1	0.9
1	160	1	20.0	0.4	0.4	2.6	2.5	1.5	2.4	-	5.9	2.5	29.9	7.9	5.7	0.4	0.9
2	200	1	19.6	0.3	-	4.2	0.3	2.3	-	3.2	2.2	2.4	30.3	8.3	6.0	0.6	0.7
3	240	1	15.7	0.6	0.4	4.6	0.1	2.5	-	4.8	-	2.7	28.3	8.6	6.5	0.7	1.0
4	280	1	13.1	0.8	0.1	4.3	-	2.5	-	4.0	-	5.8	24.0	7.5	5.6	0.8	1.4
1	200	1		0.3	-	4.2	0.3	2.3	-	3.2	2.2	2.4	30.3	8.3	6.0	0.6	0.7
2	200	1.5		0.3	0.1	4.4	0.7	2.3	0.9	2.6	2.5	2.7	30.2	7.6	5.3	0.6	1.0
3	200	3.0		0.2	0.1	3.0	1.3	1.7	1.5	2.1	2.9	2.3	29.9	8.4	5.9	0.5	0.9

Table 3. Results of the GC analysis of the products of the longterm hydrogenation test

SAMPLE NUMBER	TIME, h	TEMPERATURE, °C	VISCOSITY AT 20 °C mm <sup>2</sup> /s	COMPONENTS WITH GC RETENTION TIMES IN SECONDS, TOTAL AREA %, P=60 bar, LHSV=1 h <sup>-1</sup>													
				 269	 305	 526	 537	 733	 747	 752	 757	 771	 809	 1038	 1068	 575	 657
RPO			15.8	-	0.1	0.8	2.2	0.6	2.6	-	4.7	2.6	32.5	8.8	6.1	0.1	0.9
1	5	200	-	0.4	-	4.3	0.5	2.3	0.8	2.6	2.4	2.3	28.5	7.8	5.7	0.6	0.8
2	10	200	-	0.5	0.1	4.3	0.8	2.2	0.9	2.5	2.7	2.3	27.8	7.7	5.9	0.6	0.8
3	15	200	20.3	0.3	-	4.3	0.6	2.3	0.8	2.6	2.5	2.4	30.0	7.9	5.5	0.6	0.9
4	20	200	-	0.4	0.1	4.1	0.9	2.2	1.1	2.6	2.9	2.5	28.9	8.0	6.0	0.6	0.8
5	25	200	-	0.5	0.1	4.5	1.0	2.2	1.1	2.4	3.0	2.4	27.9	7.6	5.8	0.6	0.9
6	30	200	-	0.3	0.1	3.6	1.2	2.1	1.4	2.5	3.1	2.2	28.8	8.7	6.2	0.5	0.8
7	35	200	-	0.3	0.1	3.4	0.7	1.9	0.8	2.3	2.3	2.0	25.2	7.3	5.3	0.5	0.8
8	40	200	21.6	0.4	0.1	3.6	1.1	1.9	1.2	2.3	3.0	2.4	28.0	8.2	6.0	0.5	0.8
9	45	210	-	0.5	0.1	3.9	1.3	2.0	1.4	2.4	3.1	2.2	27.8	7.7	5.7	0.6	0.9
10	50	220	-	0.6	0.1	4.4	0.9	2.2	1.0	2.5	2.7	2.5	27.9	8.3	6.0	0.6	0.9
11	55	220	-	0.6	0.1	4.6	0.7	2.4	-	3.4	2.5	2.5	27.2	8.1	6.1	0.6	0.9
12	60	220	25.1	1.1	-	6.0	0.7	2.5	-	3.4	2.6	2.7	25.8	6.3	4.5	0.8	1.2
13	65	220	-	0.8	0.1	5.1	0.6	2.4	-	3.4	2.4	2.5	27.0	7.6	5.7	0.7	1.0
14	70	220	-	0.7	0.1	4.9	0.5	2.5	-	3.4	2.3	2.5	27.4	7.8	5.8	0.7	0.9
15	75	220	23.6	0.6	0.1	4.7	0.5	2.5	-	3.4	2.3	2.4	27.9	8.1	6.0	0.7	0.9
16	80	220	-	0.7	-	4.8	0.5	2.4	-	3.3	2.3	2.5	27.0	7.7	5.7	0.7	0.9
17	85	220	-	0.9	0.1	5.3	0.4	2.4	-	3.2	3.2	2.6	27.7	7.6	5.5	0.7	1.0
18	90	220	24.1	0.7	0.1	5.0	0.5	2.5	-	3.4	2.4	2.5	28.5	8.1	6.1	0.7	0.9
19	95	220	-	0.5	-	4.7	0.4	2.4	-	3.3	2.1	2.4	28.2	8.1	5.7	0.6	0.9
20	100	220	-	0.5	-	4.7	0.3	2.3	-	3.1	1.9	2.3	26.0	7.1	5.0	0.7	0.9
21	105	220	27.0	0.7	0.1	5.1	0.3	2.5	-	3.4	2.2	2.4	28.9	8.1	6.0	0.7	1.0
22	110	220	-	0.7	0.1	5.2	0.3	2.6	-	3.4	2.2	2.4	28.9	8.1	6.0	0.7	1.0
23	112	220	27.0	0.5	-	5.2	0.2	2.6	-	3.3	1.9	2.5	27.6	7.4	5.2	0.7	1.0

depolymerization. The temperature of 280°C was obviously too high as the undesired hydrogenation of aromatic rings took place (higher amounts of tetrahydronaphthalene at the expense of naphthalene). These results showed that the optimal effects of hydrogenation could be expected at about 220°C.

The experiments performed at 200°C also using different LHSV values showed a large influence of the liquid residence time in the reactor on the effect of hydrogenation. The LHSV values of 1.5 and especially of 3h<sup>-1</sup> were too high, and the residence time of the oil in the reactor was too small in those cases to complete the

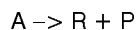
hydrogenation process. Hence, the optimal temperature and LHSV values were 220°C and 1 h<sup>-1</sup>, respectively, if the pressure was 60 bar and the H<sub>2</sub>/oil ratio amounted to 600 Ncm<sup>3</sup>/cm<sup>3</sup>.

The results of the longterm hydrogenation test are shown in Table 3. The experiment was initiated at 200°C, and after 40 hours steady-state operation, catalyst deactivation was detected. Namely, the content of indene, 4-methyl-indene and 5- and 6-methyl-indene gradually increased with hydrogenation time. That was the reason for the temperature increase, first to 210°C, however, without improvements in catalyst activity, which was the reason for further temperature increase to 220°C, when the initial catalyst activity according to GC analysis of the collected samples was re-established. A possible explanation for such an effect is that at 200°C covering of the catalyst surface by the polymerization products gradually suppresses the catalyst activity, while at higher temperatures depolymerization of the formed polymer is more favoured [4]. Moreover, a slightly higher temperature than 220°C is probably more promising, also taking into account the results of the liquid product viscosity.

The results of longterm hydrogenation test also enable analysis of the kinetics of RPO hydrogenation.

#### Determination of the reaction rate constant of catalyst deactivation

The results of the hydrogenation test during the longterm catalyst activity test at 200°C were analyzed assuming that a parallel mechanism of catalyst deactivation could be used for its determination:



where: P is polymer deposition on the catalyst surface. This type of deactivation is similar to deactivation caused by coke deposition in the process of the catalytic cracking of hydrocarbons. In this case the rate of deactivation could be expressed as [3]:

$$-\frac{da}{dt} = k_d \cdot C_A^n a^d \quad (1)$$

where: a, catalyst activity; k<sub>d</sub>, deactivation rate constant; C<sub>A</sub>, concentration of the compound which reacts with hydrogen and causes deactivation; n, d, empirical constants and exponents in the deactivation rate equation.

The mole balance of the compound denoted as A in the reactor, at the same time, could be defined by an equation taking into account that ideal plug flow exists when gas (hydrogen) and liquid (RPO) flow through the catalyst bed:

$$(-r_A) \cdot dW = G_{A0} \cdot dX_A \quad (2a)$$

or

$$(-r_A) \cdot d(W/V_0) = (-r_A) \cdot dt = C_{A0} \cdot dX_A \quad (2b)$$

where:

$$(-r_A) = k \cdot a \cdot C_A^m \quad (3)$$

In general, there are five kinetic constants: k, k<sub>d</sub>, n, m and d which must be determined. To simplify the calculation procedure and the above constant determination, it is reasonable that, according to literature values, some of these constants are:

m = 1, first order reaction with respect to the unsaturated compounds;

n = 0, the rate of deactivation does not depend on the concentration of the unsaturated hydrocarbons, and

d = 1, which is valid for the parallel mechanism of deactivation without pore diffusion resistance for reactant A (unsaturated compounds).

The experimental data based on the above assumption and quite good results were obtained after applying the corresponding procedure for the determination of k and k<sub>d</sub>.

The integral equation for a first order deactivation process defines activity as a function of time:

$$a = a_0 \cdot \exp(-k_d t) \quad (4)$$

By using equation (2), as well as the data of GC analysis regarding the content of indene (A), 4-methyl-indene and 4- and 6-methyl-indene (B and C, respectively), the deactivation rate constants were determined:

$$k_{d,A} = 1.87 \text{ h}^{-1} \quad (5a)$$

$$k_{d,B} = 0.0175 \text{ h}^{-1} \quad (5b)$$

$$k_{d,C} = 0.0107 \text{ h}^{-1} \quad (5c)$$

The above calculation were performed using the plot shown in Figure 1, assuming that under steady state conditions and oil plug flow, catalyst deactivation and hydrogenation proceed by the same first order reaction.

The obtained results showed that quite rapid catalyst deactivation occurred, and that, according to the first order deactivation model, the catalyst activity dropped to 20% of its initial value after the first 100 hours

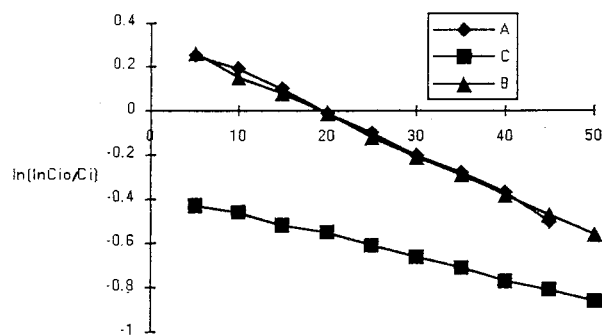


Figure 1. Dependence of  $\ln(\ln(C_{i0}/C_i))$  on time used for the calculation of the catalyst deactivation reaction rate ( $k_d$ );  $i=A$ , indene;  $i=B$ , 4-methyl-indene;  $i=C$ , mixture of 5- and 6-methyl-indene.

of hydrogenation. Increasing the temperature in the reactor from 200 to 220°C resulted in the full reactivation of the catalyst to its initial activity.

#### Determination of the reaction rate constant for indene and methyl-indene hydrogenation

The following assumptions were used for this calculation: hydrogenation is a first order reaction; the effective wetting of catalyst particles for a trickle-bed reactor indicates non-regularity of the liquid-solid phase contact [3]:

$$-\ln(1 - X_i) = k_i (\text{LHSV})^\alpha \quad (6)$$

where:  $X_i$  = conversion of compound  $i$ ;  $i = A$  (indene), B and C (4-methyl-indene and 5- and 6-methyl-indene), respectively, while  $\alpha$  represents the experimentally determined parameter which includes the catalyst wetting effect. The influence of temperature on hydrogenation was determined by using the values of the reaction rate constants obtained by performing hydrogenation with initially active catalyst ( $a_0 = 1$ ) at different temperatures. The calculated values are presented in Table 4.

Table 4. Kinetic parameters ( $A$ ,  $E/R$ ) and catalyst wetting effect compound

	$k = A \cdot \exp(-E/T)$		$k$ (593 K) min <sup>-1</sup>	$\alpha$
	$A$ , min <sup>-1</sup>	$E/R$ , K		
Indene (A)	$4.32 \cdot 10^3$	3660	2.57	-0.91
4-methyl-indene (B)	$8.43 \cdot 10^{13}$	14950	5.76	-0.65
5- and 6-methyl-indene (C)	$1.09 \cdot 10^3$	3420	1.04	-0.23

#### Determination of the reactivation rate constant when hydrogenation temperature was increased from 200 to 220°C

The results of the longterm run showed that slow deactivation of the catalyst pellets influenced the conversion degree of compounds A, B and C measured at the reactor exit. Such an effect was suppressed after 40 hours of continuous reactor operation, when the temperature inside the reactor was risen, at first to 210°C (for 5 hours) and then to 220°C for a short period of time. This is the commonly used method for stopping catalyst activity decrease, when at constant molar flow rate of the reactant, the temperature in the reactor is boosted to maintain a constant conversion degree of the reacting compounds at the reactor exit.

However, in the process of RPO hydrogenation a slow increase of the conversion degree with time was observed after the above explained procedure of temperature increase from 200 to 220°C. The increase of  $X_A$ , conversion degree (as well as  $X_B$  and  $X_C$ ) with

time was not expected if all the postulated mechanisms (first order reaction and first order deactivation) were still valid. Namely, if only increase of the reaction rate was expressed, then starting from the integral equation of the mole balance for a trickle-bed reactor:

$$-\ln(1 - X_i) = -\ln(C_{Af}/C_{A0}) = k_{i,220} \cdot a \cdot (\text{LHSV})^\alpha \quad (7)$$

one can expect, that for a constant concentration  $C_{Af}$ , at the exit of the reactor, the left-hand side of the mole balance must be constant:

$$Z = k_{i,220} \cdot a \cdot (\text{LHSV})^\alpha = k_0 e^{-E/RT} \cdot a(t) (\text{LHSV})^\alpha \quad (8)$$

However, during the longterm hydrogenation run, the values of parameter  $Z$  at 220°C slowly increased with time reaching higher and higher values in the subsequent 75 hours of the hydrogenation test when compared to the initial value when this run was started (200°C,  $a_0 = 1$ ). If the mechanism and rate of deactivation (first order) were still valid ( $a = a_0 e^{-k_d \cdot t}$ ), as well as the influence of temperature on the reaction rate constant ( $k = k_0 \cdot e^{-E/RT}$ ) and if the hydrodynamic conditions inside the reactor were unchanged ( $\text{LHSV}$ ;  $\alpha = \text{const}$ ), then the effect of the increased conversion degree of unsaturated compounds (A, indene; B, 4-methyl-indene; and C, 5- or 6-methyl-indene) could probably be related a somewhat higher catalyst activity at 220°C than expected. Such an increase of catalyst activity is probably the result of depolymerization of polymer deposits at the catalyst surface at 220°C leading to more active sites on the catalyst surface, which positively affect and increase the hydrogenation rate.

In the case of the proposed mechanism of catalyst deactivation (equation), depolymerization can be expressed as a reversible reaction:



where:

P, polymer covering the active sites of the catalyst surface and plugging the pore mouth; S, free surface of catalyst (active sites). In the sense of the reaction describing the catalyst deactivation mechanism, the process of catalyst re-activation could be expressed by the following equation:

$$-\frac{da}{dt} = k'_d \cdot (1 - a) \quad (9)$$

where: the rate of catalyst re-activation and the increase of the catalyst activity really depend on the potential, but not useful catalyst activity expressed as term  $(1-a)$  in equation (9).

Solving equation (9) with the initial condition that at the beginning of depolymerization at 220°C ( $t = t_0$ ), i.e. when when the temperature in the reactor was increased to 220°C, the catalyst activity has defined values ( $a_0 = a(t = t_0)$ ), one can obtain the change of catalyst activity with time:

$$a(t) = a' + (1 - e^{-k'_d \cdot t}) \quad (10a)$$

$$a' = a^0 e^{-k_d \cdot t} \quad (10b)$$

Such a relation and the experimental data from the longterm run at 220°C on the conversion degree for compounds A, B and C, can be used to determine the reaction rate constant of catalyst re-activation ( $k'_d$ ):

$$\ln(C_{i,0}/C_i) = k_i(220^\circ\text{C}) \cdot a(t) \cdot \text{LHSV}^{\alpha} \quad (11)$$

Or after arrangement, and taking logarithmic values of both sides of equation (11), the following linear function could be used for determining the catalyst re-activation rate constant:

$$\ln\left(\frac{1-Y}{1-a^0}\right) = -k'_d \cdot t$$

where:

$$Y = \text{LHSV}^{\alpha_i} \cdot k_i^{-1} \cdot \ln(C_{i,0}/C_i)$$

The determined values of the re-activation constants for indene and methylindene are:  $k'_{dA} = 0.011 \text{ h}^{-1}$  and  $k'_{dC} = 0.0063 \text{ h}^{-1}$ .

#### Mathematical simulation of the longterm activity test

Using the determined reaction rate constants ( $k_i$ ), as well as the deactivation rate constant at 200°C ( $k_d$ ) and reactivation rate constant at 220°C ( $k'_d$ ), the change in the conversion degree of the unsaturated compounds (indene and  $\alpha$ - and  $\beta$ -methylindene) were mathematically simulated and shown in Figures 2a, b and c. The simulation was made in two stages: the first one is the hydrogenation step at 200°C with a simultaneous deactivation process, and the second one is hydrogenation at 220°C together with catalyst reactivation or degradation of polymer deposited on the catalyst active surfaces. The degree of conversion for specific compounds was calculated by using the following equations:

$$X_i = 1 - \exp\left(-\frac{k_i(T) \cdot a(t)}{\text{LHSV}^{\alpha_i}}\right) \quad (12)$$

the first stage of the longterm test:

$$a(t) = e^{-k_d t}$$

$$X_i = 1 - \exp\left(-\frac{k_i(T) \cdot a(t,t')}{\text{LHSV}^{\alpha_i}}\right) \quad (13)$$

and, the second stage of the longterm test:

$$a(t,t') = a'(t) + (1 - e^{-k'_d \cdot t}) \quad (14)$$

The obtained experimental results and mathematical simulation showed that the initial catalyst activity was practically restored to the value  $a_0 = 1$  after about 100 hours of operation at 220°C. They also indicated that Co-Mo catalyst could successfully be applied for the hydrogenation of RPO at 220°C.

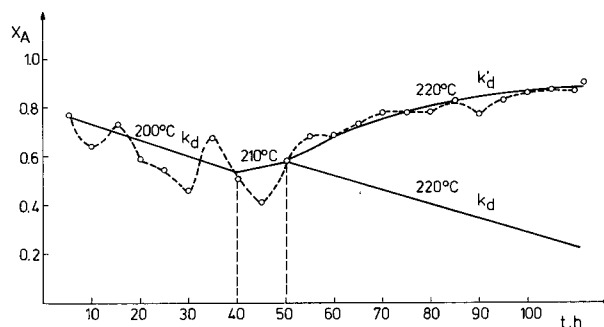


Figure 2a. Degree of conversion of indene (A) versus time; the dashed and solid lines represent the experimental and simulated curves, respectively, of the deactivation and reactivation of the catalyst (1<sup>st</sup> and 2<sup>nd</sup> stage of the longterm hydrogenation test).

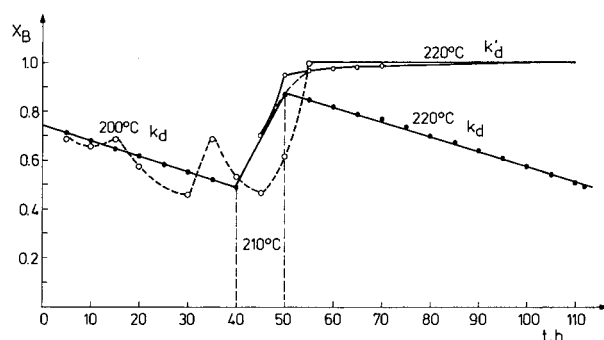


Figure 2b. Degree of conversion of 4-methyl-indene (B) versus time; the dashed and solid lines represent the experimental and simulated curves, respectively, of the deactivation and reactivation of the catalyst (1<sup>st</sup> and 2<sup>nd</sup> stage of the longterm hydrogenation test).

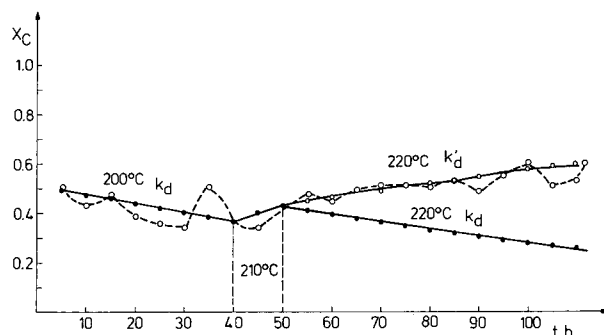


Figure 2c. Degree of conversion of 5- and 6-methyl-indene (C) versus time; the dashed and solid line represent the experimental and simulated curves, respectively, of the deactivation and reactivation of the catalyst (1<sup>st</sup> and 2<sup>nd</sup> stage of the longterm hydrogenation test).

#### CONCLUSION

The goal of the hydrogenation was to saturate the double bonds of mainly styrene and indene type compounds, thus avoiding undesirable polymerization in the residual pyrolysis oil, without hydrogenation of the aromatic rings. These tasks were achieved by performing the hydrogenation of RPO at 220–240°C with Co-Mo catalyst (BASF M8-14). The performed

experiments showed that the catalyst was deactivated very rapidly at 200°C (an 80% decrease in the catalyst activity can be expected after 100 hours at this temperature) and the lowest temperature at which the initial catalyst activity was restored was 220°C. This could be explained by the assumption that at 200°C parallel to hydrogenation, polymerization occurred, giving products which covered the catalyst surface. At 220°C and higher temperatures depolymerization prevailed over polymerization, thus restoring the initial catalyst activity. Deactivation of the catalyst, as well as the kinetics of hydrogenation were analysed by following the conversions of indene, 4-methyl-indene and 5- and 6-methyl-indene (considered as a single component), as the most representative components of

the RPO which could polymerize. Hence, the hydrogenation of 4-methyl-indene, with the relatively lowest  $k$  and  $\alpha$  values should be considered as the process which determines the overall rate of RPO hydrogenation.

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## IZVOD

### HIDROGENOVANJE PIROLITIČKOG ULJA NASTALOG U PROCESU PIROLIZE PRIMARNOG BENZINA – ODREĐIVANJE AKTIVNOSTI KATALIZATORA

(Naučni rad)

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Ispitivano je hidrogenovanje pirolitičkog ulja koje nastaje pri proizvodnji etilena (piroliza primarnog benzina, prinos 0,2 t/t). Ovo ulje ključa u intervalu temperatura 180–280°C a ima gustinu 1,05 g/cm<sup>3</sup>, i sadrži u najvećoj meri naftalen i njegove supstituisane derivate ali i druga jedinjenja stirenske, odnosno indenske strukture. Hidrogenovanjem se može sprešiti pojava polimerizacije prisutnih nezasićenih jedinjenja u ovom ulju kao što su stiren,  $\alpha$ -metilstiren, 4-, 5- and 6- metil-inden pri čemu nastaju smole sa pretežno aromatskim strukturama. Pre nego što se pristupi izdvajanju naftalena iz pirolitičkog ulja, a u cilju sprečavanja njegove polimerizacije neophodno je ovo ulje stabilizovati hidrogenovanjem. Ovo se postiže uz pomoć Co-Mo katalizatora na relativno niskim pritiscima i temperaturama (60 bar; 200–280°C).

U ovom radu ispitan je uticaj temperature i prostorne brzine na brzinu hidrogenovanja sa ciljem da se utvrde osnovni kinetički i hidrodinamički parametri pri korišćenju protočnog reaktora sa nepokretnim slojem katalizatora. Hidrogenovanje je u prvoj fazi ispitivano pri konstantnoj prostornoj brzini ulja (LHSV = 1 h<sup>-1</sup>) i odnosu vodonik/ulje (600 Nm<sup>3</sup>/m<sup>3</sup>) prateći efekte na temperaturama od 160 do 280°C. Zatim je za izabranu temperaturu (200°C) i isti odnos vodonik/ulje ispitan uticaj prostorne brzine (1, 1,5 i 3 h<sup>-1</sup>). Gasna hromatografija, GC-MS analiza i određivanje viskoziteta ulja su iskorišćeni za identifikaciju sastava pirolitičkog ulja i njegove promene tokom hidrogenovanja. Relativna stabilnost viskoziteta hidrogenovanog pirolitičkog ulja ukazuje u kojoj meri je ulje stabilizovano i sprečene neželjene reakcije polimerizacije nezasićenih aromatskih jedinjenja.

Key words: Pyrolytic oil • Hydrogenation • Catalyst activity • Deactivation • Re-activation • Mechanism • Kinetics.

Ključne reči: pirolitičko ulje • hidrogenovanje • aktivnost katalizatora • deaktivacija • reaktivacija • mehanizam • kinetika.

