

# HYDROGENATION REVIVAL OF THE PAREX REAGENT

G. Brebeanu\*, S. Neagoe and C. Savu\*\*

**abstract:** The paper presents several trials for the hydrogen revival of the PAREX reagent (concentrate of aromatic hydrocarbons), on a pilot hydrogenation station provided with a small volume of fixed layer catalyst. Three types of catalysts have been used, based on palladium, nickel and nickel-molybdenum. The desired carbonyl number has been achieved by hydrogenation of the PAREX reagent.

## 1. Introduction

The PAREX-type isomerisation facilities use a solvent composed by a concentrate of diethylbenzene-like aromatic hydrocarbons. This solvent suffers oxidation in time, thus decreasing its activity as the carbonyl number increases.

The current revival process is complicate and implies equipment very hard to control.

In order to avoid solvent loses in process, a hydrogenation revival of the solvent has been tried.

## 2. Experimental Section

The continuous flow hydrogenation revival of the solvent has been tried out on a pilot laboratory station that had a 60 cm<sup>3</sup> volume of catalyst.

The reactor is 18 mm in diameter, and is provided with a 6 mm diameter thermocouple in order to measure the reaction temperature within the catalyst layer.

The reaction conditions are as follows:

- temperature, °C: 250 – 320;
- pressure, bar: 18;
- volume rate, vol/vol.h: 1 – 5;
- hydrogen/material ratio, I<sub>N</sub> /I: 350.

The catalysts used in all experiments were manufactured in Romania.

---

\* Oil-Gas University of Ploiești, Romania

\*\* S.C. Rafinăria ASTRA Ploiești, Romania

A series of catalysts that allow easy hydrogenation, without causing any stability issues or asking for reaction severe conditions, have been studied. For this, a constant working pressure of 18 bar and a hydrogen/material ratio of 350 l<sub>N</sub>/l have been chosen, and hydrogenation temperature and volume rate have been varied.

Two solvents sampled from an industrial PAREX facility were hydrated, and three different types of catalysts were used.

The objective is to obtain by hydrogenation a decrease of carbonyl and bromine numbers, without causing any structural changes of the aromatic hydrocarbons.

The first experiment consisted in selective hydrogenation on Pd catalyst; the experimental results are shown in Table 1.

The second experiment consisted in hydrogenation of the solvent sample on a catalyst with 25.4% Ni content, within the temperature range 250 – 320°C, and a volume rate between 1 and 5 vol/vol.h. The analytical data obtained by this experiment are presented in Table 2.

Because the Ni catalyst is sensitive to sulphur compounds (it poisons easily), a third experiment has been tried out by hydrogenation of the PAREX solvent on an alumina-supported catalyst based on Ni and Mo sulphurs, similar to those used in hydro-refining and hydro-cracking. Two samples of PAREX solvent have been used and the experimental data are presented in Table 3.

The chemical composition of the analysed solvent samples, both unhydrated and hydrated, has been determined by gas chromatography.

### 3. Results and Discussions

**Table 1.** Analytical data obtained for hydrogenation of the PAREX solvent (1) on a Pd catalyst, at 18 bar, volume rate 1 vol/vol.h, and a hydrogen/material ratio of 350 l<sub>N</sub>/l

characteristic	composition mass %	unhydrogenated solvent (1)	hydrogenated solvent	
			hydrogenation temperature, °C	
			150	165
light compound		0.01	1.78	24.6
Ethylbenzene		0.01	0.21	0.35
<i>p</i> -xylene		0.11	0.13	0.36
<i>m</i> -xylene		0.39	0.37	0.87
<i>o</i> -xylene		0.60	0.53	0.89
other light compounds		6.73	6.42	4.60
<i>p</i> -DEB		37.62	26.09	37.62
<i>m</i> -DEB		38.01	39.27	30.18
<i>o</i> -DEB		4.82	4.53	3.16
unidentified compounds		11.71	11.60	8.89
bromine number, g Br/100 g product		0.40	0.20	0.20
carbonyl number, ppm		50.00	41.50	40.00

**Table 2.** Analytical data obtained for hydrogenation of the PAREX solvent (2) on a Ni catalyst, at 18 bar, and a hydrogen/material ratio of 350 l<sub>N</sub>/l

composition mass %  characteristic	unhydro- genated solvent (2)	hydrogenated solvent						
		hydrogenation temperature, °C						
		250	300	310	310	310	310	320
		volume rate, vol/vol.h						
		1	1	1	3	4	5	1
Ethylbenzene	0.02	0.11	4.45	1.23	0.11	0.10	0.08	1.10
<i>p</i> -xylene	0.13	0.17	1.69	0.79	0.18	0.20	0.16	0.41
<i>m</i> -xylene	0.41	0.54	2.65	0.85	0.47	0.50	0.59	0.49
<i>o</i> -xylene	0.62	0.70	1.54	0.29	0.68	0.68	0.63	0.30
other light compounds	6.26	6.44	14.60	3.94	3.40	10.01	9.43	22.00
<i>p</i> -DEB	36.07	34.72	11.25	6.38	33.39	35.93	34.60	15.61
<i>m</i> -DEB	39.39	36.75	11.76	7.22	39.05	36.40	37.80	17.71
<i>o</i> -DEB	4.82	4.19	1.96	1.29	4.52	4.51	4.55	2.51
other heavy compounds	12.28	16.38	49.10	78.05	18.20	11.67	12.19	62.09
Carbonyl number, ppm	47.00	11.20	7.00	0.25	0.50	0.70	1.00	1.00
Bromine number, g Br /100 g product	0.20	0.20	0.22	0.2	0.22	0.20	0.20	0.20

**Table 3.** Analytical data obtained for hydrogenation of the PAREX solvents on a Ni-Mo catalyst, at 18 bar, and a hydrogen/material ratio of 350 l<sub>N</sub>/l

composition mass %  characteristic	unhydro- genated	Solvent 1				Solvent 2			
		hydrogenated temperature, °C				hydrogenated temperature, °C			
		300	310	320	320	310	310	310	
		volume rate, vol/vol.h				volume rate, vol/vol.h			
		1	1	1	2	1	2	3	
light compounds	0.01	1.52	1.15	1.20	1.26	0.82	0.46	0.37	
Etilbenzen	0.01	0.08	0.07	0.07	0.13	0.02	2.73	4.08	4.04
<i>p</i> -xilen	0.11	0.16	0.17	0.17	0.17	0.13	0.17	0.31	0.15
<i>m</i> -xilen	0.39	0.38	0.37	0.38	0.37	0.41	0.20	0.19	0.19
<i>o</i> -xilen	0.60	0.65	0.61	0.59	0.59	0.62	0.99	1.14	1.14
other light compounds	6.73	7.78	8.54	7.77	7.78	6.26	9.47	10.15	10.34
<i>p</i> -DEB	37.62	36.25	35.5	35.55	35.70	36.07	28.26	23.19	22.41
<i>m</i> -DEB	38.01	37.39	37.13	37.80	37.80	39.39	45.33	50.79	52.52
<i>o</i> -DEB	4.82	4.09	4.19	4.45	4.04	4.82	4.35	4.81	4.67
other unknown heavy compounds	11.71	11.66	12.27	12.02	12.16	12.28	7.68	4.80	4.17
Bromine number, g Br/100 g product	0.40	0.2	0.2	0.22	0.25	0.20	0.20	0.20	0.30
Carbonyl number, ppm	50.00	1.20	1.0	0.9	1.10	47.00	0.50	0.80	1.10

Data presented in Table 1 show that the hydrogenation process at low temperature fails to hydrate the carbonyl groups as desired.

Also, the xylenes and ethylbenzene fractions significantly increase upon a 15°C increase in the temperature of the hydrogenation process.

Table 2 shows that at 250°C the hydrogenation of the carbonyl groups does not result in carbonyl number below 1 ppm level, as required. The carbonyl number decreases below 1 ppm level only at working temperatures above 300°C. The working conditions applied in this experiment allowed obtaining 0.2 g Br/100 g product for the bromine number, a characteristic value for aromatic hydrocarbons.

From the analytical data shown in Table 3 one observes that in presence of the Ni-Mo catalyst, the carbonyl number decreases to around 1 ppm, and the bromine number conforms to that required for these types of solvents.

## Conclusions

The revival of the PAREX reagent can be done easily if ones use a method that implies catalytic hydrogenation on an alumina-supported Ni-Mo-based catalyst, by applying mild reaction conditions.

The laboratory pilot station involved in hydrogenation is simple, easy to build-up and operate.

The optimal working regime for the hydrogenation of the PAREX reagent, necessary to decrease the carbonyl number below 1 ppm and the bromine number to 0.2, are:

- temperature, °C: 300 – 320;
- pressure, bar: 18;
- volume rate, vol/vol.h: 1 – 3;
- hydrogen/material ratio, I<sub>N</sub>/I: 350.

In an industrial facility, that allows a better flow regime than the laboratory pilot station, the hydrogenation can be achieved in working regime conditions milder than those used in present paper.

## REFERENCES

1. Nastasi, A. and Feyer-Ionescu, S. (1993) **Ingineria prelucrării hidrocarburilor**, vol. IV, chap. 7.1 Hidrotratate, Suci, G.C., Ionescu, C. and Feyer-Ionescu, S. Eds., Editura Tehnică, București.
2. Shiflett, W.K. and Krenzke, L.D. (2002) *Hydrocarbon Processing*, 41.
3. Reinhardt, J., Balfanz, U. and Dimmig, T. (2002) *Oil and Gas Journal*, 88.
4. Oyama, S.T., Wang, X., Requejo, F.G., Sato, T. and Yoshimura, Y. (2002) *Journal of Catalysis* **209**, 1.
5. Hartmann, J.C.M. (2001) *Hydrocarbon Processing*, 45.