

The Role of Temperature Program and Catalytic System on the Quality of Acrylonitrile-Butadiene-Styrene Degradation Oil

M. Brebu¹, M. A. Uddin, A. Muto, Y. Sakata and C. Vasile¹

Department of Applied Chemistry, Okayama University, Okayama 700-8530

¹ "P. Poni" Institute of Macromolecular Chemistry, Ro 6600 Iasi, Romania.

Introduction

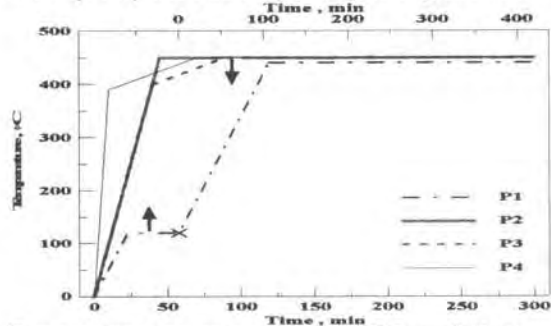
Degradation oil obtained from waste plastic can be an attractive hydrocarbon source or fuel but the presence of heteroatoms such as chlorine coming from poly(vinylchloride) (PVC) and nitrogen (N) coming from acrylonitrile-butadiene-styrene (ABS) causes problems related with the corrosion of engine parts and the formation of very harmful compounds such as HCN or NO_x as in combustion process.¹ It is very important to reduce as much as possible the amount of N-containing compounds in oils, in particular of those with complex structure as N-containing heterocycles.

Purpose of the Study

This paper presents the results obtained when different temperature programs and silica alumina/iron oxide (liquid phase contact/vapor phase contact mode) system were used for ABS thermal and catalytic degradation, respectively.

Experimental Methods

10g of ABS were thermally degraded in a glass reactor, under atmospheric pressure, by semi-batch operation, using four temperature programs. 2g of SA4 silica alumina catalyst in liquid phase contact mode (LPC) and 2g of iron oxides catalysts (γ -Fe₂O₃, Fe₃O₄-C and α -FeOOH) in vapor phase contact mode (VPC) were used for catalytic degradation.



Temperature program used for ABS degradation:

P1: room temp. → 120°C (3°C/min); hold 60 min → 440°C (3°C/min);

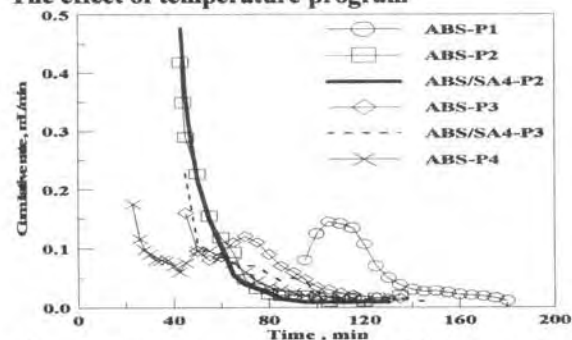
P2: room temp. → 450°C (10°C/min);

P3: room temp. → 400°C (10°C/min) → 450°C (1°C/min);

P4: room temp. → 390°C (39°C/min) → 450°C (1°C/min).

The degradation products were characterized by GC-TCD, GC-AED and GC-MS analysis.

The effect of temperature program



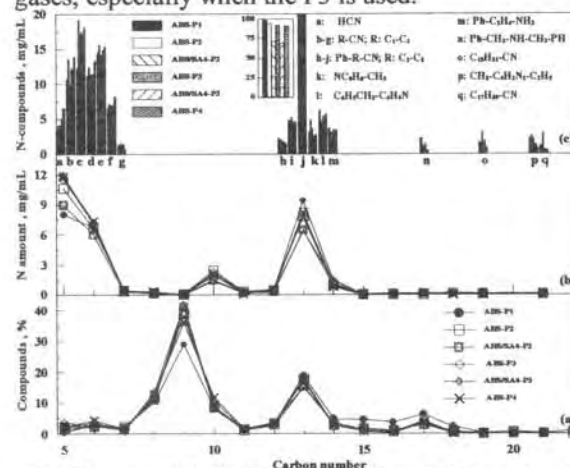
The rate of oil accumulation during ABS degradation

High heating rates increase the initial rate of oil accumulation, especially for SA4 catalyst used in LPC mode (P2 compared to P1). The oil obtained in the first moments of degradation has a dark color, showing a low quality. Using slow heating rate after degradation begins (1°C/min from 400 to 450 °C) the initial rate of oil accumulation decreases (P3 compared to P2), improving the quality of the oil.

Material Balance for ABS Degradation

method	gas (%)	oil (%)	residue (%)	oil density (g/mL)	N in oil (mg/mL)
P1	7.8	63.5	28.7	0.882	29.3
P2	7.3	63.7	29.0	0.897	31.3
SA4-P2	7.5	61.6	30.9	0.895	25.7
P3	7.0	64.1	28.9	0.890	29.0
SA4-P3	13.8	58.1	28.1	0.890	29.0
P4	6.7	63.0	30.3	0.890	31.5

High heating rates (P2-P4) cause a slight decrease in gases amount, the oil having higher density and N concentration. SA4 has a cracking effect on ABS degradation, proved by the increase in the amount of gases, especially when the P3 is used.



C-NP-gram (a), N-NP-gram (b) and the amount of N-containing compounds (c) in ABS oil

P1 program gives smaller amount of light aliphatic nitriles (n-C₅ - n-C₆) and of benzene derivatives (n-C₈ - n-C₁₀) in oil. 4-phenylbutyronitrile (n-C₁₃) and heavy hydrocarbons (n-C₁₄ - n-C₁₈) are present in higher amount. This is due to the very low heating rate and the initial pretreatment of the sample (120°C for 60 min) that allowed the cyclization of acrylonitrile units to occurs², affecting the styrene and butadiene units in ABS.³ As a result the degradation of the cyclized structure lead to formation of heavy compounds.

High heating rates increase the amount of aromatic hydrocarbons (n-C₈ - n-C₁₀) and light aliphatic nitriles (n-C₅ - n-C₆), and decrease the amount of 4-phenylbutyronitrile and heavy hydrocarbons.

SA4 increases the amount of aromatic hydrocarbons from n-C₉, and decreases the amount of almost all N-containing compounds.

The effect of catalytic system

Catalytic degradation using SA4 (LPC)/iron oxides (VPC) and P3 program was compared with thermal and catalytic degradation using only SA4 (LPC).

Material Balance for ABS Degradation

method	gas (%)	oil (%)	residue (%)	d _{oil} (g/mL)	N in oil (mg/mL)
SA4/ γ -Fe ₂ O ₃	12.3	46.2	41.5	0.863	26.8
SA4/Fe ₃ O ₄ -C	11.3	43.8	44.9	0.858	30.3
SA4/ α -FeOOH	13.9	43.0	43.1	0.856	33.9

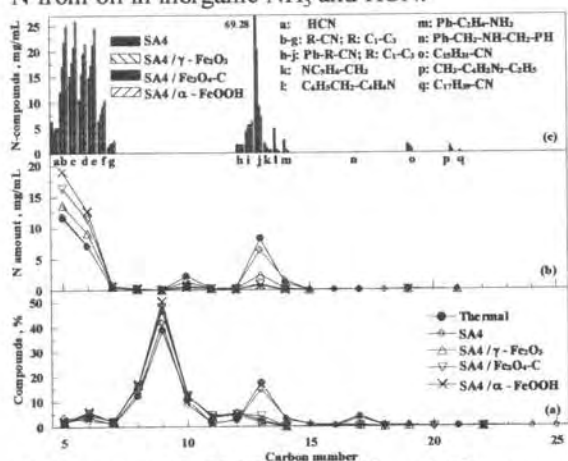
The SA4/iron oxides system decreases the amount of oil to 43-46 wt%, and also its density. High amounts of water (0.20-0.23g for γ -Fe₂O₃ and Fe₃O₄-C and 0.40g for α -FeOOH) were obtained with SA4/iron oxide catalytic system, different with ABS degradation using only iron oxides in liquid and vapor phase contact where only α -FeOOH gives traces of water.

N in degradation products (wt% of initial N)

method	NH ₃ (gas)	HCN (gas)	HCN (oil)	N _{organic} (oil)	residue
Thermal	5.07	1.27	2.92	31.37	59.37
SA4	8.59	1.95	3.56	24.90	61.00
SA4/ γ -Fe ₂ O ₃	11.84	1.47	2.09	19.46	65.14
SA4/Fe ₃ O ₄ -C	10.61	1.77	2.27	21.01	64.34
SA4/ α -FeOOH	6.29	0.81	2.20	23.41	67.29

γ -Fe₂O₃ slowly decreases the concentration of N in oil, increasing the percentage of N that goes to NH₃. Fe₃O₄-C and α -FeOOH catalysts show opposite results. For all iron oxides the amount of HCN decreases comparing with thermal or catalytic degradation of ABS using only SA4.

SA4/ α -FeOOH has the highest cracking effect, proved by the lowest amount and density of the oil. N concentration in oil has the highest value but NH₃ and HCN decreases comparing with the other iron oxide catalysts. This is different with the catalytic degradation of ABS using only iron oxides in VPC mode, where α -FeOOH favorites the conversion of N from oil in inorganic NH₃ and HCN.



C-NP-gram (a), N-NP-gram (b) and the amount of N-containing compounds (c) in ABS oil obtained with SA4(LPC)/iron oxides(VPC) and P3 program

SA4/iron oxide system significantly increases the amount of hydrocarbons from n-C₈ to n-C₁₀ (toluene, ethylbenzene, styrene, cumene, α methylstyrene) and decreases the amount of compounds heavier than n-C₁₃.

The N containing heterocyclic compounds and heavy nitriles or amino derivatives from n-C₁₄ - n-C₂₁ decreased to almost zero compared to the degradation using only SA4. The amount of 4-phenylbutyronitrile, the main N containing compound obtained from ABS degradation, decreases in oil from 17.5 wt % to 1.7-4.2 wt %. The amount of N-compounds from n-C₁₀ that we suppose to be aniline, pyridine or amino derivatives also decreases when using SA4/iron oxides. The amount of light aliphatic nitriles from n-C₅ and n-C₆ significantly increases comparing with thermal and catalytic degradation of ABS using only SA4 catalyst. These results are specific for SA4 (LPC)/iron oxides(VPC) catalytic system, because no increase in the amount of light aliphatic nitriles was observed for catalytic degradation using only SA4 or only iron oxide catalysts, with respect to the thermal degradation of ABS. We suppose that due to the cracking effect of SA4 catalyst on ABS degradation very reactive organic species appears. The secondary catalytic degradation over the iron oxides in vapor phase contact occurs easier, leading to formation of light aliphatic nitriles and a significant amount of water.

The increase in the amount of light aliphatic nitriles and the decrease of 4-phenylbutyronitrile and of the heavy N-containing compounds occurs in the order: SA4/ γ -Fe₂O₃ < SA4/Fe₃O₄-C < SA4/ α -FeOOH. Using the iron oxides in combination with SA4 catalyst causes for the Magnetite-carbon composite (Fe₃O₄-C) to exhibit higher activity than Maghemite (γ -Fe₂O₃), while for using iron oxide single catalysts they have similar activities.

Conclusions

The amount and the quality of the oil obtained from thermal degradation of ABS by semi-batch operation depends on the heating rate, the final temperature of degradation and the residence time of the polymer and the products in the reactor.

The degradation of the ABS wastes was performed with good results for converting the heavy and heterocyclic N-containing compounds into light aliphatic nitriles, by using high heating rates (10 or 39 °C/min) until the degradation begins, followed by slowly heating (1 °C/min) until the final temperature for degradation of 450 °C.

The use of the SA4(LPC)/iron oxides(VPC) catalytic system gives better quality oil than single catalyst use. The main hydrocarbons (toluene, ethylbenzene, styrene, cumene, α -methylstyrene) increases in amount and the distribution of nitrogen in oil is changed from heavy aliphatic nitriles to light aliphatic ones. SA4/ α -FeOOH system gives best results in ABS degradation, the amount of 4-phenylbutyronitrile decreasing from 17.5 to 1.7 wt % and the N-containing heterocyclic and heavy compounds being completely removed from the oil.

References

- Özdoğan, S.; Uygur, S. Eğrican, N. *Energy* **1997**, *22*, 681-692.
- Xue, T. J.; McKinney, M. A.; Wilkie, C. *Polym. Deg. Stab.*, **1997**, *58*, 193-202.
- Vasile, C.; Cascaval, C. N.; Ilie, A.; Schneider, I. *A. J. Thermal. Anal.* **1979**, *15*, 141-150.