CHEMICAL RECYCLING OF WASTE HYDROCARBONS IN CATALYTIC CRACKING

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Abstract

The possibility of the chemical recycling of waste hydrocarbon fractions, e.g. waste polymers or waste lubricating oils in catalytic cracking was verified in the MAT laboratory test. Linear 1-olefins were used as model compounds simulating products of thermal pre-cracking of waste polyolefins into liquid fraction suitable for admixing to HVGO as standard FCC feed, and products of semi-pilot plant thermal/catalytic cracking of industrial PP wastes were used as possible real feed. Filtered used automotive oil was tested as possible feed to catalytic cracking to chemical recycling. A standard FCC catalyst was used in microactivity test at 525°C, introduction time of 40 s and catalyst/feed ratio of 4.76 g/g. No negative effect in coking was observed as consequence of olefinic fraction adding to hydrogenated VGO feed. Similarly, the use of thermally/catalytically pre-cracked fraction in pilot-plant treatment of industrial polypropylene wastes showed good possibility of chemical recycling of waste polyolefines in FCC process into gases and gasoline fraction. Catalytic cracking of used automotive oil increased conversion to gases and gasoline with little increase of Gas Factor after longer use of this oil. Results showed good possibility for chemical recycling of waste polymers and waste lubricating oils in FCC technology into gases and gasoline.

Keywords: waste plastics, used oils, catalytic cracking

1. INTRODUCTION

Waste hydrocarbons represent a serious problem in everyday life. The greatest quantities of waste hydrocarbons are mainly waste plastics and also used lubricating oils. Both these wastes come from crude oil and even if both could be used for energy production by incineration, the best way for they treatment should be the material or chemical recycling.

Polymer wasted could be regarded as potential source of chemicals and energy. Different methods of polymer wastes recycling are developed [1,2]. One of the most attractive ways is chemical recycling that converts waste polymers into basic monomers or petrochemicals. About 60-70% of waste polymeric materials are composed of PE and PP that cannot be easily converted into monomers.

For chemical recycling of waste polymers a thermal or catalytic method could be applied, by which the long alkyl chains of polymers are broken into a mixture of lighter hydrocarbons [3-20].

One of the most appropriate chemical recycling of used polyolefins is fluid catalytic cracking process that could convert waste polyolefines directly into fractions of light olefins and motor fuels. The main problem is the state of waste polyolefines – they are available in form of greater or smaller pieces or in powder – all as solids which could not be simply added to FCC feed – hydrogenated WGO. The best way to introduce the polyolefin feed to FCC process is admixing of thermally depolymerized polymers in liquid state to the base FCC feed – hydrogenated vacuum gas oil [3]. The research in this

field is focused to use of solid acid catalysts as natural or synthetic zeolites. To the main types of reactors used for the laboratory catalytic depolymerization belong batch reactor [4-6] but examples from flow-type reactors are known [7-9]. Many experiments were carried-out in thermobalances (TGA) with mixtures of about 10 wt. % of catalyst with plastics [10-16]. The best possibility gives laboratoty simulation of fluidized-bed reactors [3, 17-19] of MAT-tests.

As heterogeneous catalysts, different mesoporous acid catalysts as conventional amorphous alumosilicates [4] and different microporous molecular sieves – zeolites of types USY [6,7,12,15,16], ZSM-5, [4-7,10-15,19] BEA [10], MOR [10] as well as mesoporous molecular sieves of MCM-41 type [8,13,14,19,20], and commercial FCC catalysts [3,15-18] were tested. Generally, the catalytic depolymerization is carried out over acid catalysts in atmosphere of nitrogen or other inert gas. Consequently, the cracking products are strongly non-saturated, and catalysts are deactivated because of coking. Catalytically pre-cracked polyolefines contain mainly linear and branched unsaturated and alkane molecules and aromatics. The olefins in feed represent the main different between such feed for FCC and standard feed for FCC, represented by HVGO.

The paper deals with the study of the treatment of liquid and solid waste hydrocarbons – mainly waste plastics and waste lubricating oils – in catalytic cracking processes of treatment of petroleum fractions- FCC mainly to fraction of gases and motor fuels – gasoline.

2. EXPERIMENTAL

In the present work the influence of additives of model compounds, representing examples of thermally depolymerized polyethylene, were studied. As model compounds were used 1-olefines C_6–C_{24} pure and in 10% additives to standard FCC feed – hydrogenated vacuum gas oil. Tests were carried-out in Micro-Activity Test (MAT) at 525°C. The treatment of long 1-olefins increases the total micro-activity values - conversion to gases and gasoline. As industrial example of pre-cracked polymer wastes, liquid product of thermal decomposition of polypropylene wastes in Blowdec process [21] was studied. As feed representing waste oils was tested used lubricating oil from diesel engine in bus.

2.1. Feeds:

A) Hydrogenated Vacuum Gas Oil (HVGO)
As feed for MAT was used a standard refinery feed for FCC from refinery - hydrogenated vacuum gas oil (HVGO). Its basic properties are summarized in Table 1.

Table 1 Properties of Hydrogenated Vacuum Gas Oil (HVGO)

density (20 °C)	906 kg/m3
viscosity at 50°C	43.41 mm2/s
viscosity at 100°C	8.436 mm2/s
distillation	
SD	322 °C
10% vol.	385 °C
30% vol.	436 °C
50% vol.	473 °C
70% vol.	506 °C
90% vol.	541 °C
ED	555 °C
Sulphur	0.033 wt. %
Nitrogen	1002 ppm wt.
Nikel	0.01 ppm wt.
Vanad	0.07 ppm wt.
Sodium	0.01 ppm wt.
Iron	0.22ppm wt.
Melting point	40 °C

B) Pure LAO - Linear alpha-olefins (Spolana Neratovice, Czech republic) with the carbon chain of 6, 8, 10, 12, 14, 16, 18, 20-24, were used as model compounds of the polyolefins thermal depolymerization. The purity of LAO was 98.4 % wt.

C) Mixture of 10 wt. % of individual LAO in HVGO was prepared by mechanical mixing of HVGO and LAO at temperature of 50°C.

D) Product of pilot-plant thermal/catalytic depolymerization of industrial polypropylene wastes, realized in Blowdec equipment [21], denoted as PP- BLW.

Table 2 Properties of depolymerized polypropylene wastes PP-BLW

kin. viscosity at 40^0C, mm^2/s	5.797
kin. viscosity at 20^0C, mm^2/s	53.36
density at 15^0C, kg/m^3	819.2
density at 20^0C, kg/m^3	815.4
bromine number, g Br/100g	56.1
sulfur, mg/kg	98
nitrogen, mg/kg	305
Distillation (vol.%):	
SD	92.3 ^{0}C
5	154.4 ^{0}C
10	179.4 ^{0}C
20	224.4 ^{0}C
30	265.3 ^{0}C
40	308.1 ^{0}C
50	342.8 ^{0}C
60	357.3 ^{0}C
70	358.6 ^{0}C
ED	358.7 ^{0}C
Aromatic carbon,	7 wt.%
Parafinic carbon	54 wt.%
Naftenic carbon	39 wt.%

E) Waste automotive oil LD SAE 15W-40 used in diesel engine in bus of following properties (before filtering) in Table 3

Table 3 Properties of waste automotive oil LD SAE 15W-40

Density:	899 kg/m^3
Sulfate ash:	1.05 wt. %
Sulphur:	0.494 wt. %
Mechanical impurities:	0.23 wt. %
Metals content:	
Zn	1 421 mg/kg
Ca	1 858 mg/kg
Na	286 mg/kg
Mg	238 mg/kg
Fe	61.1 mg/kg
Al	25.8 mg/kg

2.2. Catalytic test

For laboratory catalytic cracking tests of above-mentioned feeds was used microactivity test (MAT) according to ASTM D-3907-92 [22].
Reaction conditions in MAT:
Temperature: 525°C
Catalyst weight: 4.00 ±0.005 g
Introduction time: 40 s
Catalyst/Feed: 4.76 g/g
Total flow of nitrogen: 30 ml/min

2.3. Catalyst

As cracking catalyst, a commercial equilibrated FCC catalyst from refinery was used with acidity value by TPDA of 0.150 mmol of acid center/gram and surface area of 140 m^2/g. The main characteristics of used FCC catalyst are in Table 4, its SEM picture is in Figure 1. Before MAT tests, 4 g of catalyst was calcined at 560 °C for 3 hrs.

Table 4 Characteristics of FCC catalyst

Catalyst	S_{BET} (m^2/g)	*S_t (m^2/g)	*V_{micro} (cm^3/g)	V_{total} (cm^3/g)	**Acidity (mmol a.s./g)
FCC equilibrated	140	49.4	0.042	0.182	0.150

* S_t and V_{micro} calculated by t-plot method, ** Acidity determined by TPDA

2.4. Analytical methods

Products of the conversion of microactivity tests were separated as liquid and gaseous products. Liquid products were collected by freezing at 0°C.

Liquid and gaseous reaction products of microactivity tests were analyzed by GC. For analysis of liquid products, HP-1 column (25m x 0.2 mm x 0.33μm) with split-injection was used; composition of hydrocarbons in gaseous products was measured in PONA column (50m x 0.2 mm x 0.5μm), both by GC HP5990A Series II with FID-detector. Molar ratio of hydrogen to methane (Gas-Factor) was determined by GC HP5990A Series II with TCD-detector using packed column with PORAPAK Q (1.8m x 2 mm) at 25 °C.

The value of microactivity (MA) was determined according to ASTM D-3907-92 as a portion of feed converted to products with boiling point lower than 216°C – gases and gasoline fraction.

3. RESULTS AND DISCUSSION

3.1. Conversion of olefinic feeds and pre-cracked PP-wastes

Fig.2 shows examples of GC-analysis of liquid products of conversion of standard feed – hydrogenated vacuum gas-oil HVGO (2a), HVGO with 10 wt. % of LAO-6 (2b), and pure LAO-18 (2c). From the GC-analysis it is seen that the spectra of liquid products are in all cases essentially the same; only the composition of HCO (liquid product with boiling point over 343°C) in the case of pure LAO-18 is simpler. Similarly, the GC-spectra of gaseous products of the conversion of standard feed were basically the same as in the case of conversion of pure LAO, differences were in the quantitative composition.

Microactivity for standard feed (HVGO), standard HVGO with 10% LAO (10% LAO$_6$ – LAO$_{18}$), pure LAO (LAO$_n$), depolymerized PP wastes (PP-BLW) and 10% in HVGO (10%PP-BLW), gas factor and coke are in Figs. 3-5. As it is seen from Fig. 3, microactivity (MA – conversion of feed into gaseous products and liquid with b.p. up to 216°C) increase after addition of pure olefinic molecules and fractions to standard HVGO-feed. The increase of MA is quite logical for 1-olefins in comparison with HVGO because the LAO feeds are generally lighter than HVGO. For LAO 6 – 12 one could propose that MA value should be 100 %, because the feeds have boiling point under 216 °C. But as it is seen from Fig. 3, even during catalytic cracking of LAO6 also hydrocarbons with boiling point over 216°C (C_{12}) were created by condensation and aromatization reactions (MA=88.4). By the increase of chain length of LAO from 6 to 10 MA even little decreased but it is still higher than those of pure HVGO.

For pure olefinic feeds C_{18} and C_{18-24} the microactivity value MA (conversion of feed into gas and naphtha) increased from 82.5 for HVGO feed to 97. For product of thermal pretreatment of polypropylene wastes the microactivity achieved value 90 for pure PP-BLW fraction and 84.2 for 10% of this fraction in HVGO. Generally, mixtures of 10% of all these olefinic feeds with standard HVGO increased MA to about 85-90 in comparison with 82.6 for pure HVGO.

There was not observed increased hydrogen creation as coking indication (Gas Factor – Fig. 4) and no higher coke formation (Fig. 5) after conversion of mixture of 10% of linear 1-olefines with standard HVGO nor in the case of their use as pure feed. The coke content for tested feeds and mixtures was generally 1.5-1.7 wt. % in comparison with 1.9 wt.% for pure HVGO.
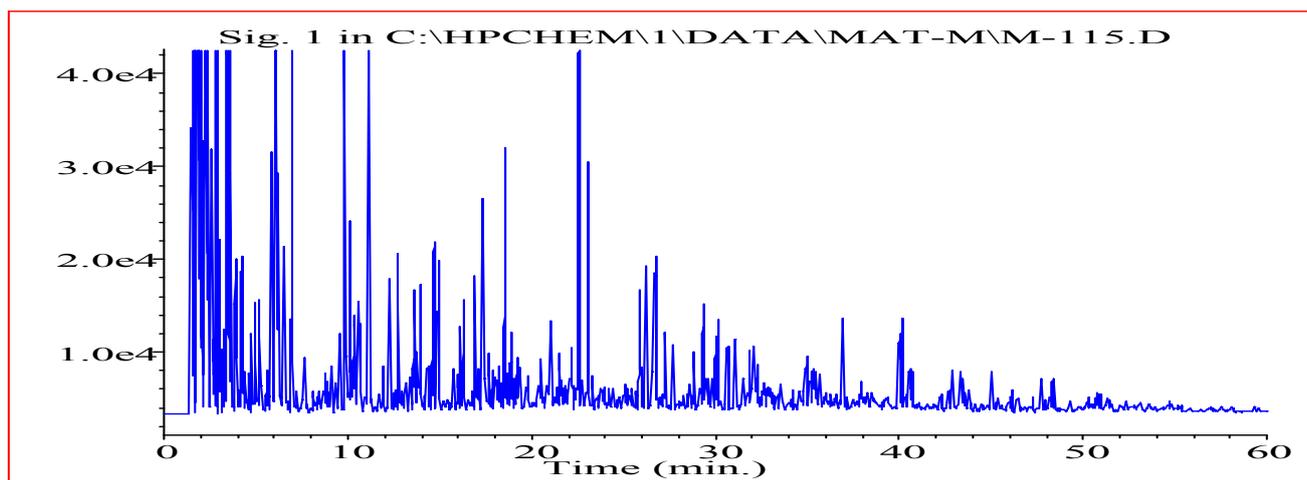
2a) Standard feed-HVGO
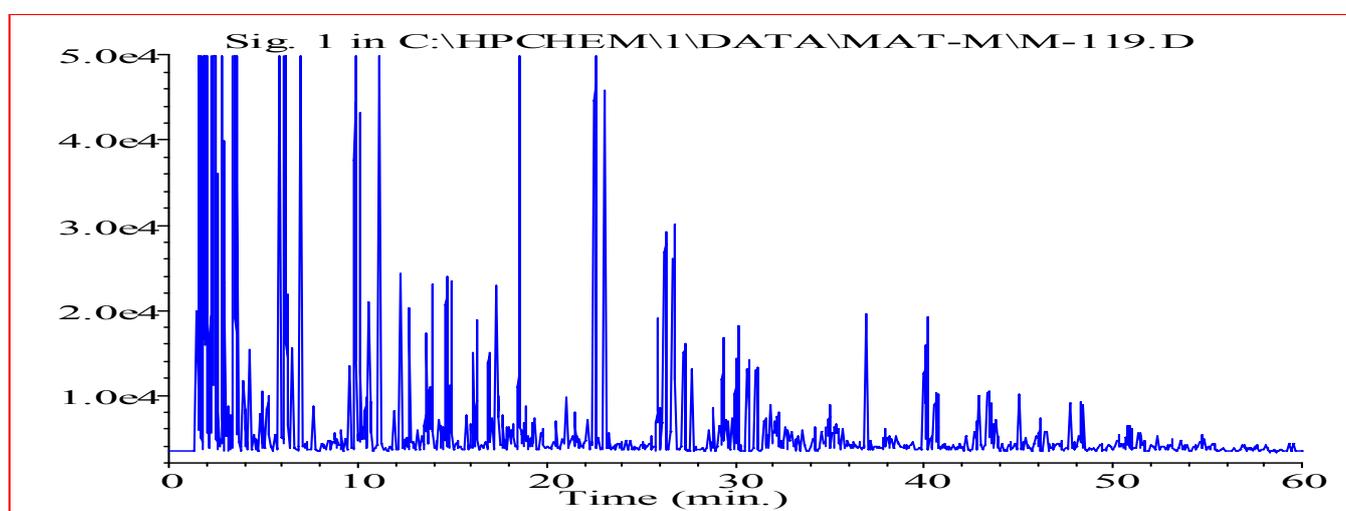
2b) HVGO + 10% wt. LAO-C6
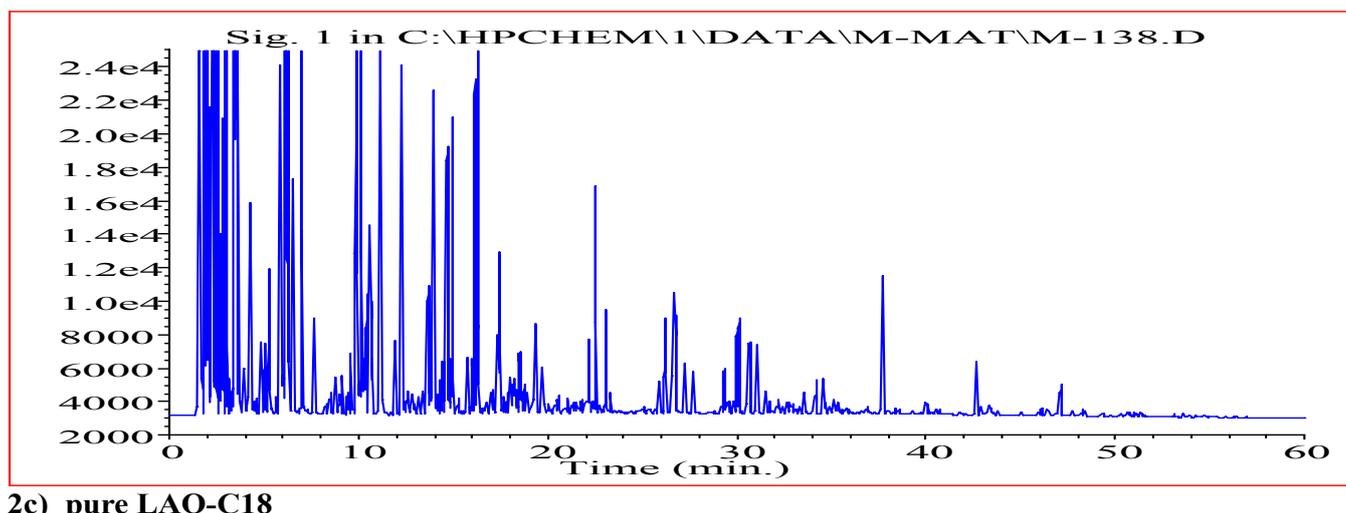
2c) pure LAO-C18

Figure 2 Examples of GC analysis of liquid products of MAT for different feeds (retention time of n-C_{12} with b.p. 216°C is 19.8 min, retention of n-C_{20} with b.p. 343°C is 42.7 min)
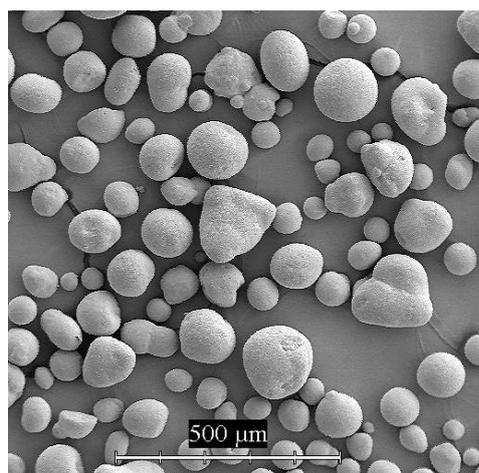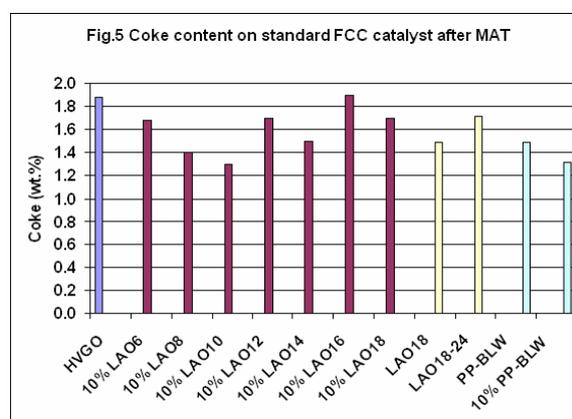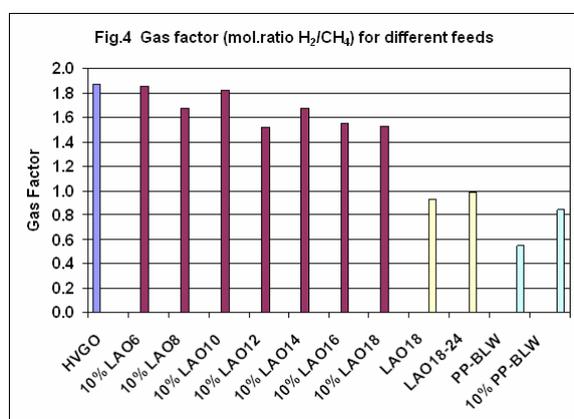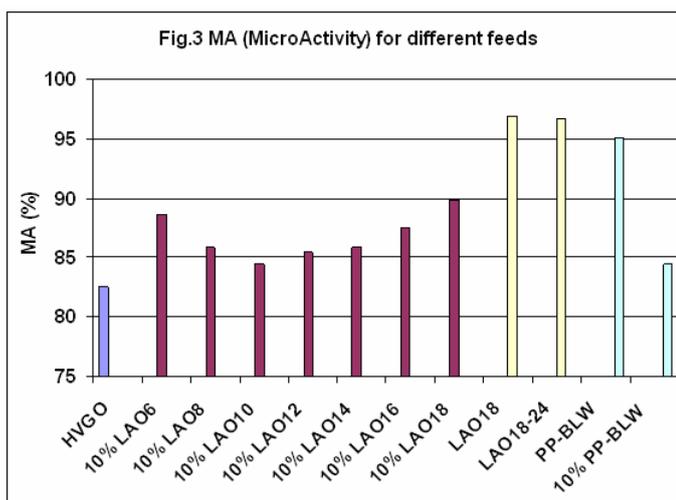
Figure 1. SEM of used FCC catalyst

3.2. Conversion of waste automotive oil

Results of MAT tests of mixture of 10 wt.% of waste oil with HVGO showed a little improve in total conversion into fuels (MA) as well as in smaller coke formation. The composition of gases C_2-C_5 (ratios olefin:paraffin and ratios iso:n) was almost unchanged.
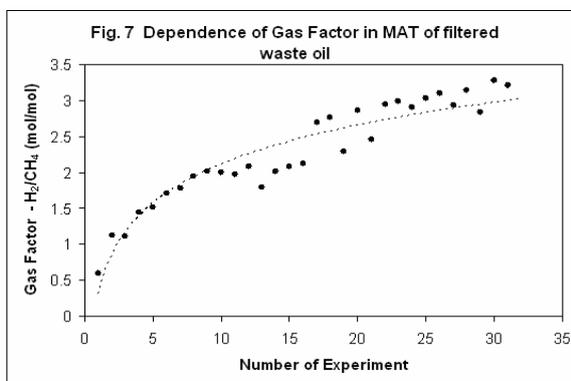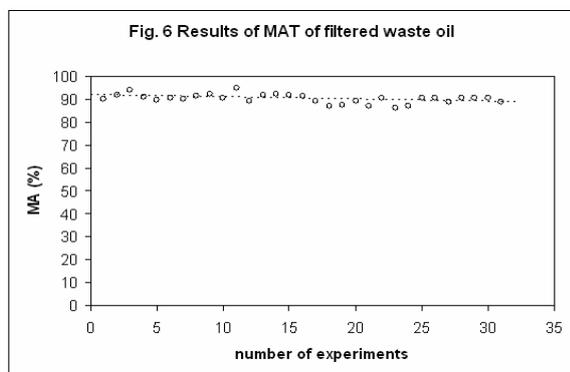
Table 5 MAT results using HVGO and various feeds with filtered waste oil

Feed	MA	GF	Coke (wt.%)	Gaseous products composition					
				$C_2^=/C_2$	$C_3^=/C_3$	$C_4^=/C_4$	$C_5^=/C_5$	iC_4/nC_4	iC_5/nC_5
HVGO	82.6	1.86	1.88	1.37	3.58	0.59	0.26	5.02	16.08
10% of filtered waste oil/ HVGO	82.9	1.68	1.55	1.58	3.57	0.65	0.27	5.18	16.10
Filtered waste oil*	88.5	0.60-3.20	1.39	2.15	5.05	0.55	0.28	8.01	16.6

*Average values from 30 experiments

Because the waste oil contains higher quantities of various metals, as it is seen in Table 5, we verified the influence of possible poisoning of FCC catalyst after the conversion of higher quantities of waste oil. For the verification of possible influence of the conversion of greater quantities of waste oil we repeated the MAT-experiments with fresh feed – pure waste oil over the same 4g of catalyst. The results in Fig. 6 show that after more than 30 MAT experiments with filtered waste oil over the same catalyst the value of microactivity (MA) was practically the same, maybe only with tiny decrease. Also the composition of gaseous products giving greater ratio of olefin/paraffin at C_2 and C_3 and greater iC_4/nC_4 than at pure HVGO did not changed with the experiment number. The coke quantity was during all repeated experiments about 1.40 wt. %, lower than

1.86 wt. % at HVGO. Only one value increased during experiments – Gas Factor (molar ratio of H_2/CH_4) – Fig. 7. The explanation could be in the increased depositions of metals from waste automotive oils with the increased quantity of treated waste oil. But it is necessary to realize that in practical technological conditions the waste oils could represent only a few wt. % from total feed, based on HVGO.

Fig. 6 Results of MAT of filtered waste oil

Fig. 7 Dependence of Gas Factor in MAT of filtered waste oil

4. CONCLUSION

Microactivity tests of catalytic cracking of olefinic compounds and fractions representing model compounds of thermal pre-cracking of waste polymers to liquid form suitable for admixing to standard FCC feed showed positive effect to cracking activity to gasoline and gases (MA) with no-negative effect in coking. Similarly it was shown that it is possible to treat the waste automotive oils in FCC process in small additives to basic feed – HVGO and to convert it to gases and fuels. Even if the above-mentioned successful tests were carried out with 10% additives of 1-olefins or thermally cracked plastics and with pure waste oil, in real conditions such feeds could contain only a few wt. % of waste oil or unsaturated products of pre-cracking polymers and the possible negative influences to FCC process seems to be negligible. The treatment of pre-cracked waste polyolefins as well as used oils in FCC represents attractive possibility of chemical recycling of such waste hydrocarbons into olefinic monomers and FCC gasoline

Acknowledgements

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