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Periodica Polytechnica Chemical Engineering

Upgrading of Waste Tyre Pyrolysis Oil for Obtaining Valuable Products

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Abstract

Pyrolysis (thermal anaerobic decomposition) of waste tyres is a sustainable recycling process. Its result is an unstable liquid product – pyrolysis oil – must be improved for economic usage. A complex microreactor system was developed for upgrading/valorizing waste tyre pyrolysis oil. Following cleaning steps (distillation, resin removal, chemical preparation reactor) pyrolysis oil was hydrogenated/hydrodesulfurized in the main reactor over $NiMo/Al_2O_3$ catalysts. Cheap self-made low active metal containing catalysts presented comparable activities with an industrial (Haldor Topsoe) catalyst in a 100 mL flow reactor at 300 °C temperature and 25–35 bar pressure. The process was optimized by changing the pressure, the liquid hourly space velocity (LHSV) and the hydrogen flow rate. The upgrading of the process for a 1000 mL volume flow system is in progress.

Keywords

waste tyre, pyrolysis oil upgrading, NiMo catalyst

1 Introduction

Waste tyres are present in huge amount (up to 5×10^6 ton/year worldwide [1]), their disposal and utilization is necessary. Mostly waste tyre recycling remains at physical level (ground rubber after retreading [2]), their combustion will emit a large number of environmental pollutants, such as SO_2 and polynuclear aromatic hydrocarbons (PAH) [3].

The best solution for environmentally friendly recycling of used tires is the pyrolysis of waste tires. Pyrolysis is the thermal anaerobic decomposition of organic compounds into less complicated ones with lower molecular weights. Gases (volatiles), liquids (tars) and solids (chars) are produced in the process. Waste tyre pyrolysis oil (WTPO) is a dark brown/black liquid and its economic use is unsolved. WTPO is a mixture of various hydrocarbons with carbon atoms of C_5–C_{20}: paraffins, olefins, diolefins, (poly)aromatic hydrocarbons and monoterpenes [4–7].

Natural rubber is a polymer consisting of chains of isoprene molecules. One of the main thermal decomposition products of polyisoprene is limonene. Limonene is widely used in the perfumery, cosmetics, food and pharmaceutical industries. It is a precursor for the synthesis of other organic compounds, such as menthol. Technical limonene is an excellent solvent used in the plastics, paints, and varnishes, automotive and construction industries. Thermal degradation of limonene leads to aromatic derivatives of BTEX (benzene, toluene, ethylbenzene, xylene) [8].

Pyrolysis oils without further treatment cannot be used directly as fuels. Due to their high aromatics content their octane number is high and cetane number is low. Modern vehicles need highly stable, not prone to resignification gasoline, therefore they cannot be operated with pyrolysis oil due to its instability. The higher boiling compounds of pyrolysis oil are valuable diesel fuel components, but moisture and olefins must be removed, aromatics content need to be decreased and desulfurization of the oil is necessary [9].

Apart from the gasoline and diesel fractions separated by distillation [10], other valuable products can be produced from the oil by catalytic hydrogenation (HYD)/hydrodesulfurization (HDS) [11], oxidative desulfurization (ODS), ultrasound-assisted oxidative desulfurization (UAOD), and acid treatment [12]. Sulfided $NiMo/Al_2O_3$ catalysts are generally used at temperatures of 300 °C or higher to stabilize and valorize the pyrolysis oils [13, 14].

The active metals utilized in HDS are predominantly Mo(W) and Co(Ni) mostly in bimetallic combination. Alumina supported CoMo catalysts are the best in HDS, due to their high HYD activities NiMo combination is generally used in hydrodenitrogenation, saturation of aromatics and deep HDS, NiW active phases are mainly in hydrocracking catalysts [15, 16].

The Palota Environmental Protection Ltd. developed a microreactor system for treating/valorizing waste tire pyrolysis oils (Fig. 1). The initial results were published elsewhere [17].

2 Experimental methods

Sphere and cylinder shaped gamma alumina supports were provided by SASOL. These γ-Al$_2$O$_3$ supports were co-impregnated by aqueous solutions of Ni(NO$_3$)$_2$ and (NH$_4$)$_6$Mo$_7$O$_{24}$. After impregnation the catalysts were dried and then calcined at 500 °C for 2 h. The compositions of the calcined catalysts were Ni/(Ni+Mo) = 0.3 molar ratio and 10 wt% MoO$_3$ contents. The commercial NiMo/Al$_2$O$_3$ catalyst (HyBRIM) with much higher active metal (Ni and Mo) content than our self-made catalysts were provided by Haldor Topsoe. The oxide form catalysts were activated by *in situ* sulfidation with dimethyl-disulfide added in gas oil to a total sulfur content of 3 wt% S at a final temperature of 350 °C. The reaction was carried out over 100 mL catalyst in a flow reactor at 25, 30 and 35 bar pressures and at 300 °C reaction temperature, at 0.5–1.5 liquid hourly space velocity (LHSV) and at

Fig. 1 Schematic diagram of the microreactor system

0.2–0.6 L/min hydrogen flow rate conditions. The compositions of pyrolysis oils and their product mixtures were measured by GC-MS using an Agilent 6890 GC and 7893 A MS equipped with a HP-PONA 50 m 0.2 mm 0.50 μm GC column. The samples were diluted with CS$_2$ and toluene and chlorobenzene solutions were added as internal analytical standards. These mixtures were directly injected into the GC. The concentrations were calculated from the GC peak areas, therefore they can be regarded as approximate wt% values only. The reacted/original peak area ratios are more reliable values. X-ray photoelectron spectroscopy (XPS) measurements of used catalysts were performed in a KRATOS XSAM 800 instrument equipped with an atmospheric pretreatment chamber and using an unmonochromatized Al K$_\alpha$ source (1486.6 eV). The Al 2p binding energy from the alumina support set at 74.4 eV was used as reference for charge compensation. The samples were heated in air at 200 °C for 2 h before XPS measurements.

3 Results and discussion

The raw pyrolysis oil gained from different commercial sources was initially distilled, then the distillate was further cleaned in a resin remover, then in a chemical pretreatment reactor before entry in the main hydrogenation/desulfurization reactor as indicated in Fig. 1. The yield of the distilled oil with respect to the raw oil was about 60–70%.

All compounds identified by GC-MS in the cleaned and upgraded pyrolysis oil with their boiling points are shown in Table 1. Alkanes, alkenes, aromatics, thiophenes and limonene are the main components and the compounds with boiling points up to 205 °C are valuable additives to gasoline, those with higher boiling points to diesel oil (Table 1).

The compositions of the cleaned pyrolysis oil and its product mixture over the sphere shaped 10 wt% MoO$_3$ containing NiMo/Al$_2$O$_3$ catalyst at LHSV = 1/h and 0.2 L/min hydrogen flow during 7 days reaction time are shown in Fig. 2. The initial composition of the oil was 4% alkanes and alkenes, respectively, 57% aromatics, 34% limonene and 1% thiophenes. Following 1 day reaction it changed to 13% alkanes, 2% alkenes, 82% aromatics, 1.4% limonene and 0.7% thiophenes and remained more or less stable up to 7 days (Fig. 2). The compositions over the commercial catalyst under the same conditions (except the shorter, 4 days reaction time) presented similar values and stabilities (Fig. 3). Direct comparison is not possible as the original compositions of the initial pyrolysis oils were different.

As the compositions of the product mixtures were quite stable for several days, the averages of daily concentrations were studied afterwards. The effect of LHSV over the
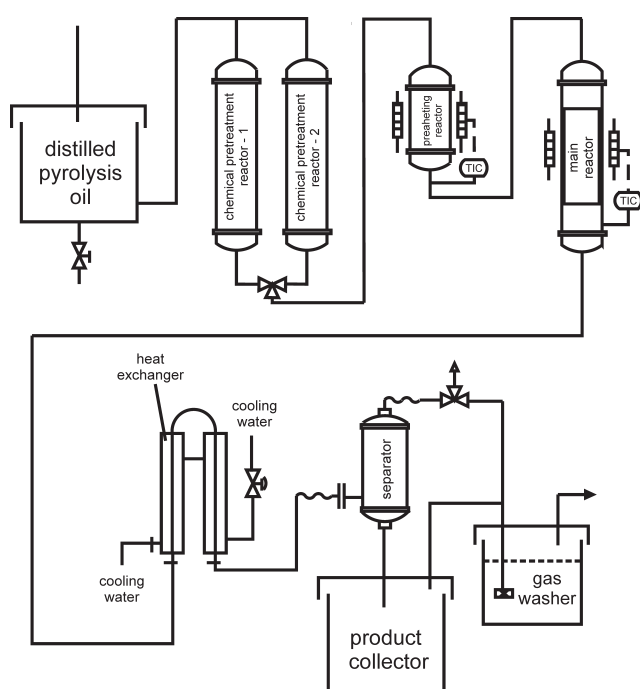
Table 1 All identified compounds in the cleaned and upgraded pyrolysis oil with their boiling points

Alkanes	Boiling point (°C)	Alkenes	Boiling point (°C)	Aromatics	Boiling point (°C)
n-Hexane	69	1-Hexene	63	Benzene	80
n-Heptane	98	3-Methyl-2-Pentene	69	Toluene	111
n-Octane	126	1-Heptene	94	Ethylbenzene	136
n-Dodecane	216	Diisobutylene	101	*p*-Xylene	137
n-Tridecane	235	1-Octene	121	*m*-Xylene	139
n-Tetradecane	253	1-Dodecene	213	*o*-Xylene	144
n-Hexadecane	287	1-Tridecene	232	Styrene	145
n-Heptadecane	303	1-Tetradecene	251	Indane	176
n-Octadecane	317	1-Hexadecene	274	Indene	182
n-Nonadecane	330	1-Heptadecene	300		
n-Eicosane	343	1-Octadecene	315	Thiophenes	
Cyclopentane	49	1-Nonadecene	329	Thiophene	84
Cyclohexane	81	1-Eicosene	341	2-Methylthiophene	113
		Cyclopentene	44	Tetrahydrothiophene	121
Limonene	176	Methylcyclopentene	72	2-Ethylthiophene	132
		Cyclohexene	83	2,3-Dimethylthiophene	138
		Methylcyclohexene	110		
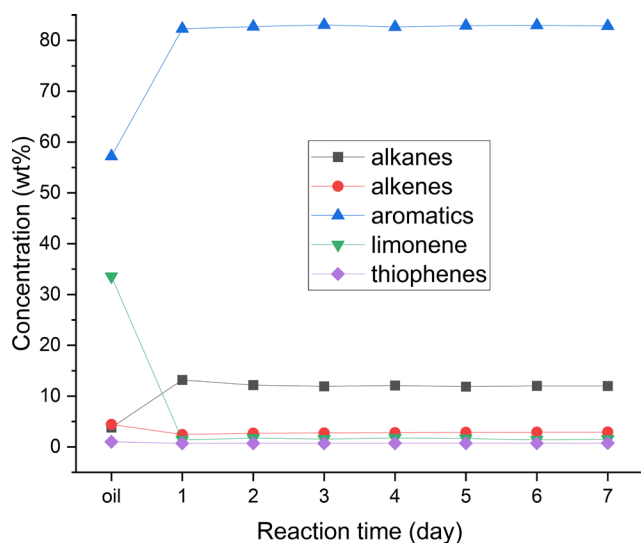
Fig. 2 Composition of the pyrolysis oil and its product mixture over the sphere shaped NiMo/Al$_2$O$_3$ catalyst at 30 bar pressure, LHSV = 1/h and 0.2 L/min hydrogen flow conditions
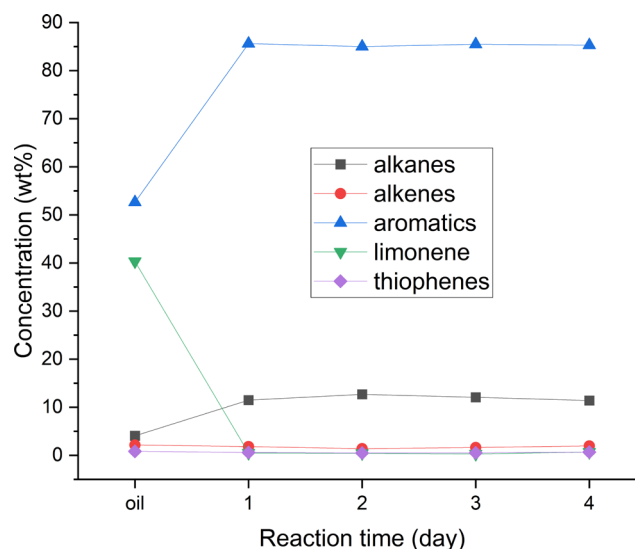
Fig. 3 Composition of the pyrolysis oil and its product mixture over the commercial NiMo/Al$_2$O$_3$ catalyst at 30 bar pressure, LHSV = 1/h and 0.2 L/min hydrogen flow conditions

sphere shaped and commercial catalysts are presented on Figs. 4 and 5, respectively. It is quite clear that the main reaction is the production of aromatics from limonene in agreement with the literature [8]. The average daily concentrations of aromatics are more or less stable at every studied space velocity. Only the concentration of alkanes decreases systematically from 18% at LHSV = 0.5 to 9% at LHSV = 1.5 over the sphere shaped catalyst (Fig. 4) and from 15% (LHSV = 0.75) to 10% (LHSV = 1.5) over the commercial catalyst (Fig. 5). The 3–4 wt% alkene content

of the oils decreases to roughly 1 wt% at the lowest space velocities and slightly decreases at the highest ones (Figs. 4 and 5). Consequently, probably alkanes are produced from limonene, alkenes and thiophenes in a decreasing order.

The effect of increasing hydrogen stream rate was also studied over the sphere shaped (Fig. 6) and commercial (Fig. 7) catalysts. The averages of daily aromatics concentrations were very stable (83%) over the sphere shaped catalysts and decreased from 85 to 79% over the commercial catalyst with increasing hydrogen flow rates.
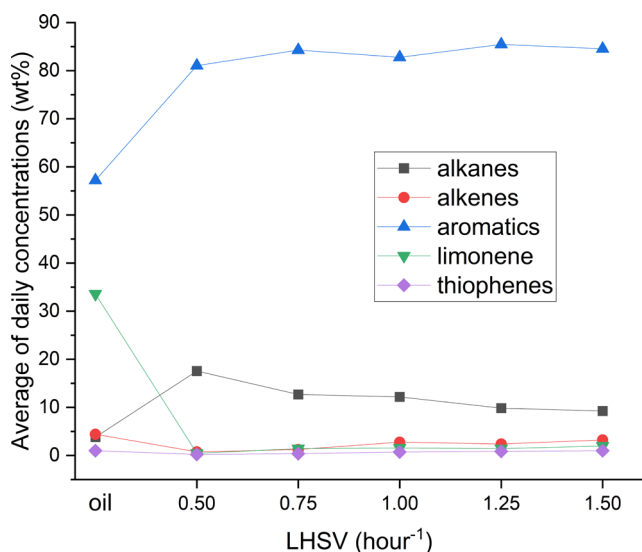
Fig. 4 Composition of the pyrolysis oil and average of daily concentrations of its product mixture at different space velocities over the sphere shaped NiMo/Al$_2$O$_3$ catalyst at 0.2 L/min hydrogen flow rate
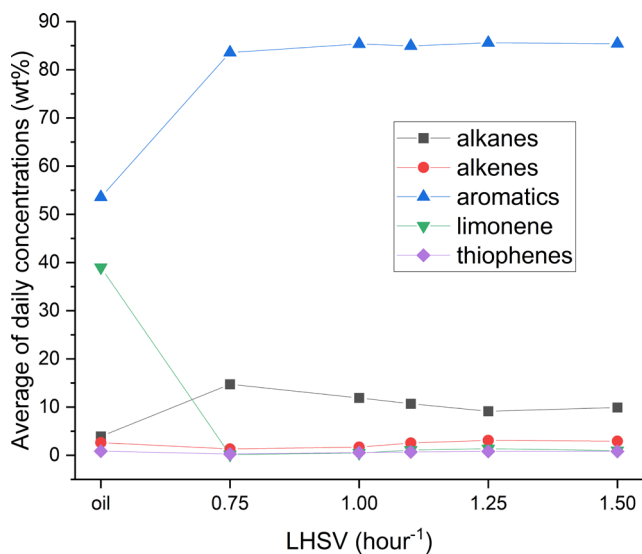

Fig. 6 Composition of the pyrolysis oil and average of daily concentrations of its product mixture at LHSV = 1/h and different hydrogen stream rates over the sphere shaped NiMo/Al$_2$O$_3$ catalyst

Fig. 5 Composition of the pyrolysis oil and average of daily concentrations of its product mixture at different space velocities over the commercial NiMo/Al$_2$O$_3$ catalyst at 0.2 L/min hydrogen flow rate conditions

Fig. 7 Composition of the pyrolysis oil and average of daily concentrations of its product mixture at LHSV = 1/h and different hydrogen stream rates over the commercial NiMo/Al$_2$O$_3$ catalyst

Table 2 Ratios of average daily concentrations related to oil compositions over the sphere shaped NiMo/Al$_2$O$_3$ catalyst

LHSV (1/h)	0.5	0.75	1	1	1	1.25	1.50
H$_2$ (L/min)	0.2	0.2	0.2	0.4	0.6	0.2	0.2
Alkanes	4.38	3.00	3.19	3.47	3.22	2.46	2.31
Alkenes	0.20	0.53	0.63	0.71	1.00	0.84	1.13
Aromatics	1.45	1.55	1.45	1.50	1.50	1.54	1.52
Limonene	0.01	0.04	0.05	0.01	0.01	0.04	0.05
Thiophenes	0.21	0.43	0.72	0.61	0.72	0.95	1.09

Accordingly, the alkane contents were stable and increasing (from 12 to 19%), respectively, over the sphere and commercial catalysts.

In order to get real concentration ratios, the averages of daily GC peak areas of product groups were divided by the GC peak areas of the corresponding compound groups in the oil, these values are presented in Tables 2 and 3. It is clearly seen that the relative concentration increase of alkanes was the highest among all compound groups,
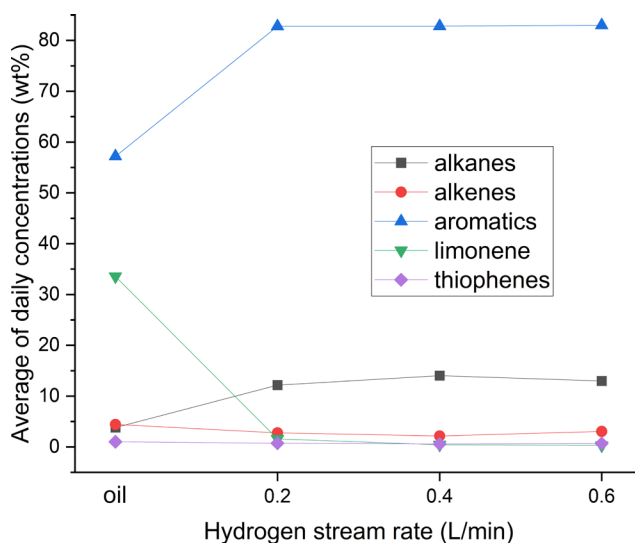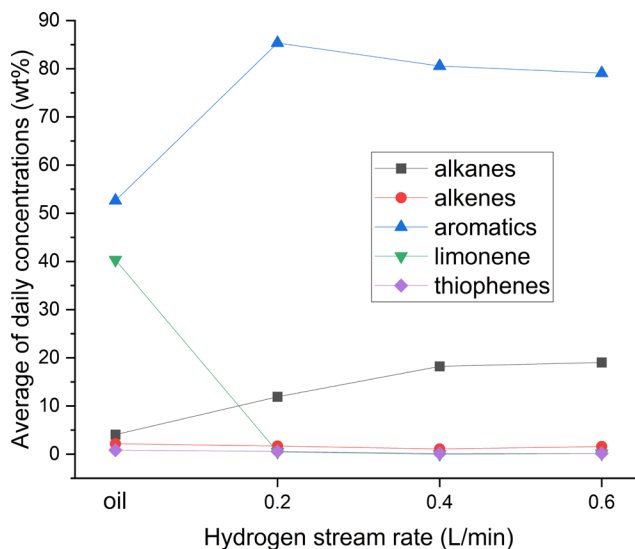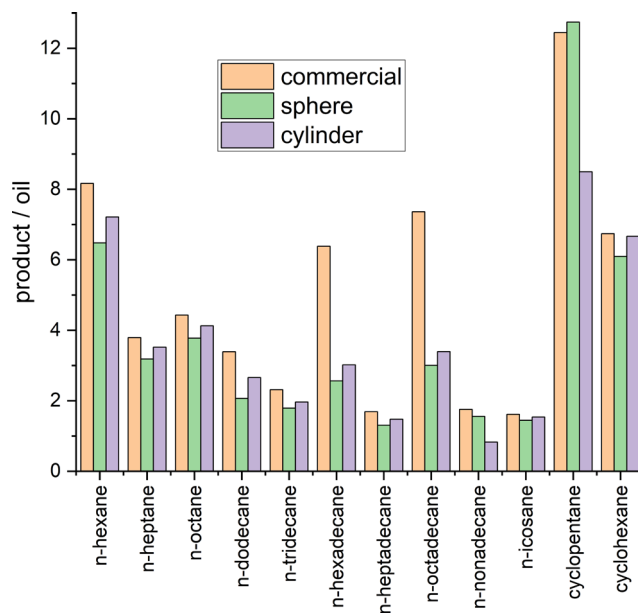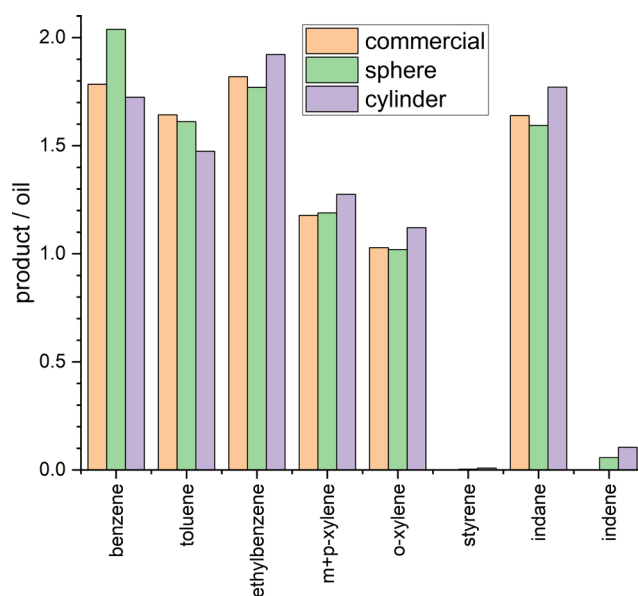
Table 3 Ratios of average daily concentrations related to oil compositions over commercial NiMo/Al$_2$O$_3$ catalyst

LHSV (1/h)	0.75	1	1	1	1.25	1.50
H$_2$ (L/min)	0.2	0.2	0.4	0.6	0.2	0.2
Alkanes	3.89	2.93	4.48	5.02	2.41	2.62
Alkenes	0.42	0.79	0.50	0.51	0.99	0.94
Aromatics	1.53	1.62	1.53	1.45	1.57	1.57
Limonene	0.00	0.01	0.00	0.00	0.04	0.03
Thiophenes	0.31	0.67	0.17	0.17	0.90	0.89

the concentrations of aromatics increased with roughly 50%, and limonene practically disappeared under every reaction conditions. The only characteristic difference between the self-made and commercial catalysts is the much higher alkanes concentration ratios related to the oil composition in the latter at LHSV = 1 and 0.6 hydrogen flow rate conditions (compare 3.22 in Table 2 with 5.02 in Table 3). Low LHSV and hydrogen stream rates are the most beneficial for the hydrogenation of alkenes and hydrodesulphurization of thiophenes, which were the main objectives of the project, but they do not disappear completely. Nevertheless, we chose LHSV = 1/h and 0.2 L/min hydrogen gas stream values at 30 bar pressure for practical operation conditions to avoid plugging due to resin formation, etc.

Apart from the standard 30 bar pressure, experiments were also carried out at 25 and 35 bar pressures, but characteristic effects in reaction product compositions were not found between the different catalysts, therefore these results are not presented here.

Ratios of the most important individual compounds over commercial, sphere- and cylinder-shaped catalysts sorted as alkanes, aromatics and alkenes-limonene-thiophenes are presented in Figs. 8–10, respectively. These are real concentration ratios and the increase of alkane (especially cyclopentane, cyclohexane and n-Hexane) ratios are 2–12 fold (Fig. 8), those of aromatics (BTEX and indane) are 1–2 fold (Fig. 9), which means that hydrogenation activities of all catalysts are quite good. All alkene ratios over the commercial catalyst and with two exceptions (cyclopentene and methylcyclohexene) also over the self-made catalysts are below one (Fig. 10). Limonene disappears almost completely during the reaction and the conversion of thiophenes is more than 60% over the commercial and around 20–35% over our self-made catalysts. The most important finding is that the hydrogenation activity of the self-made (sphere and cylinder shaped) catalysts is comparable with the one of the commercial catalyst.

Fig. 8 Ratios of average daily alkane concentrations related to oil compositions over commercial and self-made catalysts measured under LHSV = 1/h, H$_2$ stream = 0.2 L/min and p = 30 bar reaction conditions

Fig. 9 Ratios of average daily aromatics concentrations related to oil compositions over commercial and self-made catalysts measured under LHSV = 1/h, H$_2$ stream = 0.2 L/min and p = 30 bar reaction conditions

The XPS spectra of the used commercial and sphere shaped catalysts (Figs. 11–13) revealed that the active metals (Ni and Mo) are mostly (60–80%) sulfided and the commercial catalyst contains halogens (chlorine and bromine) on its surface. A detailed analysis is not possible due the high extent of impurities (carbon and oxygen) on the surface of both catalysts.
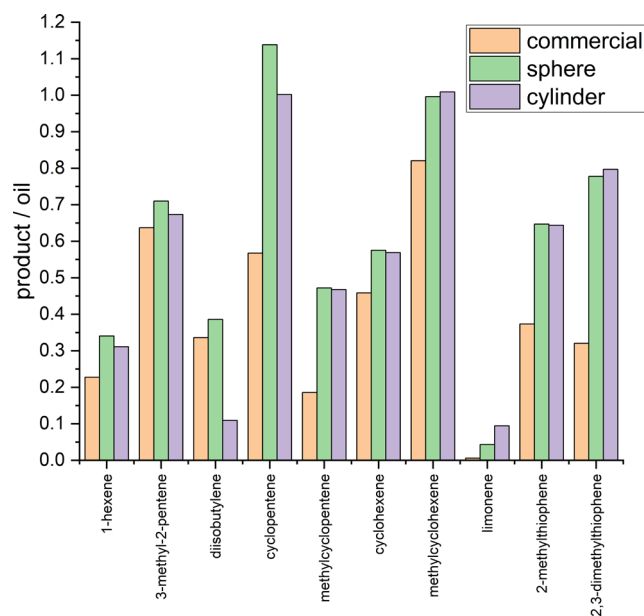
Fig. 10 Ratios of average daily alkenes, limonene and thiophenes concentrations related to oil compositions over commercial and self-made catalysts measured under LHSV = 1/h, H_2 stream = 0.2 L/min and p = 30 bar reaction conditions
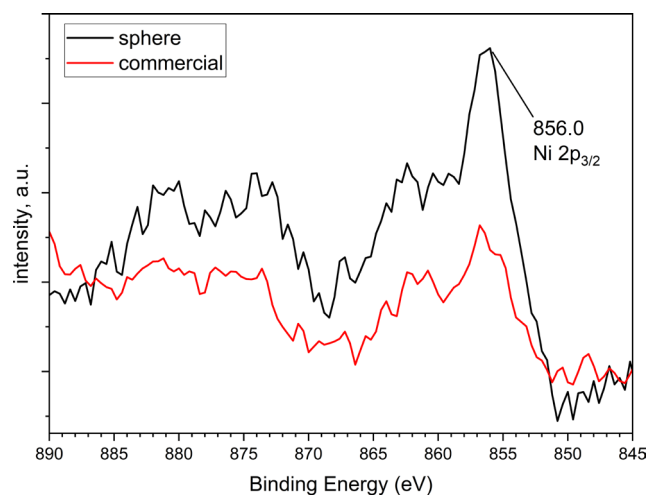

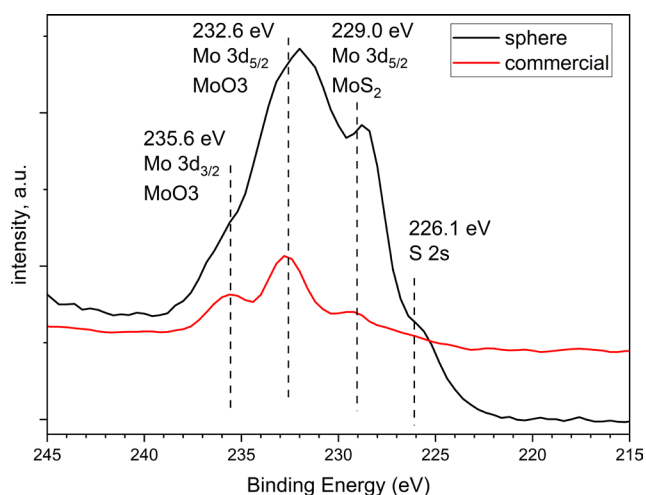Fig. 11 Ni 2p XPS spectra of commercial and sphere shaped used catalysts

Fig. 12 Mo 3d and S 2s XPS spectra of commercial and sphere shaped used catalysts
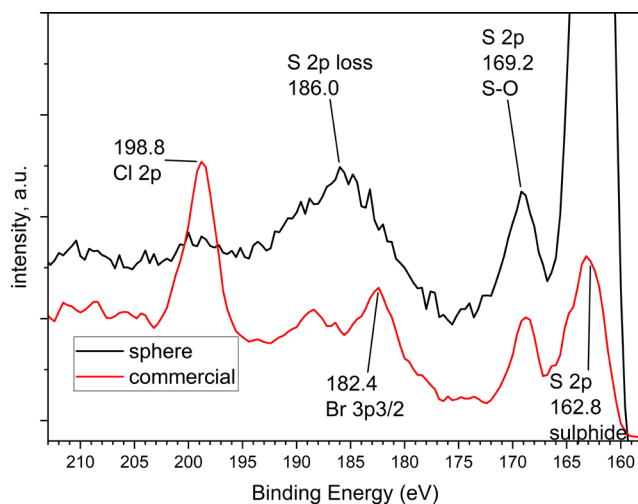
Fig. 13 Cl 2p, Br 3p and S 2p XPS spectra of commercial and sphere shaped used catalysts

4 Conclusion

The catalytic activity of self-made catalysts was comparable with the activity of the commercial, much higher active metal containing NiMo/Al$_2$O$_3$ catalyst at least at low temperature and pressure. Neither catalysts showed any remarkable deactivation even after one-week long operation time. Limonene is a valuable compound in the original pyrolysis oil, its separation should be considered before the hydrogenation treatment. Due to their high concentrations in the product mixture aromatics (Benzene-Toluene-Ethylbenzene-Xylene, BTEX) are the most valuable products of the process. Alkenes and thiophenes cannot be hydrogenated completely in our process neither over the commercial catalyst, but the properties (stability and colorless) of the pyrolysis oil remarkably improved.

We emphasize the importance of discovering the halogen content of pyrolysis oils, therefore they should be dehalogenated before catalytic hydrogenation/desulfurization. It will be important to carry out further experiments to optimize dehalogenation, to deal with sedimentation problems, and in connection with further developments in technology and control. Our development goals are aimed at developing a more complex, multi-reactor system.

Acknowledgement

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