

Production of Low-Aromatic Light Blending Components by Hydroprocessing of Heavy Biomass-Based Gasoline

David Graf ^{a)}, Philipp Neuner ^{b)} and Reinhard Rauch ^{c)}

Karlsruhe Institute of Technology (KIT), Engler-Bunte-Institute, Department Fuel Technology (EBI-ceb), Engler-Bunte-Ring 1a, 76131 Karlsruhe, Germany

^{a)}Corresponding author: David.Graf@kit.edu

^{b)}Philipp.Neuner@kit.edu

^{c)}Reinhard.Rauch@kit.edu

Abstract. The number of internal combustion vehicles annually registered in Germany continues to outstrip that of electric cars, which will be continually dependent on fuel supplies. Those ambitious goals are disclosed by the European Green Deal, which not only calls for new technical approaches but also for greenhouse gas-neutral transition technologies. For the transportation sector, such bridging technologies are synthetic fuels, e.g., utilizing the bioliq[®] process for a CO₂-neutral gasoline supply. To be used in existing engines, such fuels must be adapted to the applicable national standards. Hydroprocessing is a suitable process by which parameters can be variably adapted to requirements. In this work, we considered heavy aromatic-rich gasoline, separated from the product of the bioliq[®] process by distillation. We investigated how to selectively modify the boiling behavior to make the product suitable as a high-quality blending component. Over a wide range of temperature and pressure, we utilized three commercially available Pt-supported catalysts. We were able to achieve high gasoline yields, while the content of low-end compounds up to a boiling temperature of 150 °C could be increased significantly. In contrast to the heavy character of the produced gasolines, the octane numbers obtained were in a satisfactory range. Especially the MON turned out unexpectedly high and showed a clear dependence on the iso-paraffin content. Thus, this study deals with improving the standard compliance of synthetic MtG and DtG fuels.

INTRODUCTION

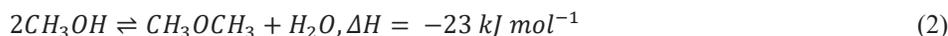
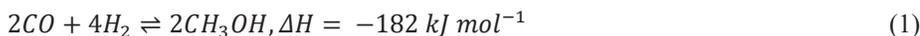
The global climate crisis as the greatest challenge of the present has underlined the urgency of a rapid expansion of renewable energies and the associated reduction of greenhouse gas (GHG) emissions. Many countries are starting to transform their energy sector towards greater sustainability, including the European Union with the Green Deal [1]. The transformation aims to comprehensively create a CO₂-neutral economy and society by 2050, with a focus on the sustainable use of available raw materials while preserving biodiversity [2]. This concept addresses all sectors of the energy system, of which the transport sector contributes about 18 % to the total GHG emissions [3]. Vehicles with electric and fuel cell drive systems (or a combination of both technologies) are currently considered the most promising technologies for decarbonizing the traffic sector in the medium term [4]. However, the average lifetime of a car in Germany is 18 years [5]. In addition, the share of sales with combustion engines still exceeds the electric driven one. According to official statistics from the Federal Motor Transport Authority, in 2020, vehicles with electric drive systems counted only 6.7 % for fully electric and 6.9 % for hybrid vehicles on German roads [6]. Therefore, the ambitious climate targets can only be achieved if a GHG neutral alternative can be provided for the vehicles that will still rely on an internal-combustion engine. A quasi-CO₂-neutral drive technology based on synthetic fuels is an essential transition technology. A different situation is emerging in the transportation and aviation sector, which are dependent on energy sources with high energy densities. The share of synthetic fuels in these sectors will largely depend on progress in other technologies, such as electromobility. Due to these uncertainties, it is important to continue researching synthetic fuels as potential alternatives [3] and to develop concepts for their supply. Since synthetic fuels are to be used in existing engines, an important subject is to adjust the gasoline quality according to

national standards. In this work, the hydroprocessing of a heavy gasoline is investigated. The fraction is rich in aromatics and was separated by distillation beforehand. The suitability of the obtained product to improve the quality of the bio-based fuel by a possible back-blending is studied. The focus is particularly on the boiling characteristics, since methanol-to-gasoline (MtG) and dimethyl ether (DME)-to-gasoline (DtG) fuels generally do not meet the standard in this regard.

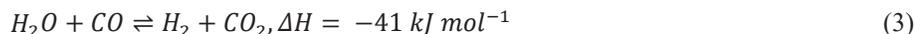
PROCESSES FOR SUSTAINABLE GASOLINE SUPPLY

To produce synthetic gasoline various common process approaches exist. The routes considered in this study are MtG and DtG, which are indirect catalytic processes utilizing methanol and DME, respectively. Both processes are based on Mobil Oil's discovery in the 1970s that methanol can be catalytically converted to higher aromatics via a ZSM-5 zeolite [7]. The ZSM-5 zeolite has pores of medium size at relatively high acid strength, which determines its selectivity to form products in the boiling range of gasoline [8].

The DtG synthesis offers an economic advantage compared to the indirect synthesis with methanol as an intermediate product due to lower investment costs and hence higher profit [9]. Furthermore, the increased economic efficiency results from the sequential reactions involved. The methanol formed in the equilibrium reaction (1) reacts directly to form DME in reaction (2), which accelerates the conversion of the synthesis gas because of the constant removal of the intermediate product methanol [10].



In addition, the water formed during DME formation is converted with carbon monoxide through the water-gas-shift (WGS) reaction (3). The result is a further increase of the driving force because the hydrogen formed is in turn involved in the methanol synthesis [11].



Consequently, the methanol conversion is higher and thus the resulting recycling flow is lower, which in turn can reduce operating costs [12]. The feasibility of the direct DME synthesis has already been demonstrated by companies such as JFE Holdings Inc. and Haldor Topsøe A/S [13]. The bioliq[®] process developed at the Karlsruhe Institute of Technology (KIT) allows the conversion of low-grade lignocellulosic biomass such as residual wood or straw to synthetic fuels via entrained flow gasification followed by a DtG-process [13,14].

Synthetic Gasoline and Associated Challenges

The similar product spectra of the MtG and DtG processes consist of paraffins, olefins and mostly methylated aromatics [15]. Ranging from C₆ to C₁₀, the aromatic distribution shows a maximum at C₈ [15]. With the bioliq[®] pilot plant a very high overall aromatics content of >75 wt.% is achieved, resulting in a relatively low proportion of light ends [16]. The characteristically high aromatic content is accompanied by an increased octane number, which makes such fuels suitable for gasoline engines [7,15]. Due to the reaction mechanism also heavy aromatics like 1,2,4,5-Tetramethylbenzene (durene) are formed. The high melting temperature of 79 °C can cause precipitation of solid durene at cold conditions and consequently clog fuel injection systems [17]. Depending on the synthesis conditions, the product contains 3 – 6 wt.% of durene, whereas for fossil gasoline the concentration is only 0.2 – 0.3 wt.% [7]. However, laboratory tests showed satisfactory engine performances with durene concentrations in the range of 2 – 4 wt.% [7,17,18]. In a bio-refinery, there are two main strategies for adjusting the required maximum concentration. By implementing a dosing unit, it is possible to add the synthetic gasoline to a refinery stream in a defined quantity and thus adjust the durene concentration. Another option is the separation by distillation, whereby a light and heavy gasoline are obtained, the former being directly used as gasoline or blending component. The advantage of this process variant is the possibility for a simultaneous improvement of the emission behavior during engine combustion. The reason is the removal of large aromatics, which have a greater tendency to form soot [19,20]. The sooting behavior is expressed in the literature by parameters such as the Threshold Sooting Index or the novel Yield Sooting Index [21].

These parameters can be used to derive a possible procedure for processing the separated heavy gasoline. In principle, naphthenes and paraffins tend to form less soot [22].

UPGRADING OF A GASOLINE RICH IN HEAVY AROMATICS

Origin and Composition of the Feedstock

The gasoline synthesized in the bioliq[®] process consists of up to one third of heavy gasoline. In an atmospheric distillation, the gasoline is separated into a light and heavy fraction at a condenser temperature of approx. 170 °C. The heavy gasoline rich in durenene is forwarded to a treatment process, which is the subject of this study. Table 1 shows that almost 97 wt.% of the feedstock is aromatic in nature. With a share of approx. 52.6 wt.%, the largest part consists of C₁₀ (21,4 wt% durenene) and approx. 10.4 wt.% of C₁₂₊ aromatics. Furthermore, the C₉ aromatics are the second largest proportion with 33.8 wt.%. The remaining 3 wt.% are mostly naphthenic in nature. Due to the bioliq[®] process route operated with an additional gas cleaning step, the syngas and thus the gasoline is free of sulfur.

TABLE 1. General conditions for otto-fuels according to the DIN EN 228 [23] in comparison to the bioliq[®] light and heavy gasoline after distillation.

Parameter	Unit	DIN EN 228	Light gasoline bioliq [®]	Heavy gasoline bioliq [®]
RON	–	min. 95	101.7	n.a.
MON	–	min. 85	93.7	n.a.
Density	kg m ⁻³	720.0 – 775.0	828.91	891.72
Vapor Pressure (Class A)	kPa	45 – 60	31 ± 3	0.15 ± 0.07
E70	vol.%	22.0 – 50.0	1,1 ± 0,3	0.0
E100	vol.%	46.0 – 72.0	6.4 ± 0.3	0.0
E150	vol.%	75.0	85.4 ± 0.3	0.0
Final Boiling Point	°C	210	171 ± 2	290 ± 2
Benzene	vol.%	max. 1.00	1.63	0.0
Olefins	vol.%	max. 18.0	1.14	traces
Aromatics	vol.%	35	76.28	96.52
Oxygenates	wt.%	3.7	traces	0.0

Hydroprocessing – Hydrogenation and Hydrocracking of Aromatics

For the upgrading of hydrocarbon mixtures to optimize petrochemical properties, hydroprocessing is frequently referred to in literature. Depending on the application, the term hydroprocessing is used for different reactions, for example hydrogenation, hydrocracking or hydroisomerization. Which reaction pathways and thus catalysts are most promising for a given feedstock strongly depends on the target parameters and how they are to be changed.

The permissible limits for mono ring and polycyclic aromatic hydrocarbons (PAHs) have been tightened in recent years and will probably be further restricted by additional environmental regulations. Mono cyclic, and especially polycyclic ones, have a particularly strong tendency to form soot, as this is influenced by the substance group and the size of the molecule [24].

In gasoline fuels, aromatics are associated with a high octane number and are thus principally desirable. However, a higher content, especially of large aromatics, leads to more emissions of engine-out hydrocarbons [25]. Modern automotive catalytic converters operate at a high level of efficiency and can remove up to 97 % of CO and engine-out hydrocarbon emissions. However, the operation below the so-called “lightoff” temperature is problematic. Depending on the emissions under consideration, it is approx. 250 °C. [26] The time period between the cold engine start-up and reaching the catalyst’s operating temperature can be responsible for a large portion of the hydrocarbon emissions. According to the Federal Test Procedure (FTP), more than 60 % of hydrocarbon emissions occur during this period when simulating a drive in an urban environment. [27]

As mentioned above, the heavy gasoline from the bioliq[®] process will be upgraded and blended back into the light gasoline to compensate for disadvantages. The parameters adjusted by the upgrading process are determined by

comparing the light gasoline with the specifications of DIN EN 228 (see Table 1). In particular, the E-values of the light gasoline are too low. They indicate which volume fraction has evaporated at a certain temperature during a distillation. For example, the measured value for parameter E70 is defined as the volume fraction evaporated at 70 °C. Equally, the aromatics content significantly deviates from the permitted limit of 35 vol.%. The density and vapor pressure do not meet the standard, but the difference is still tolerable. Considering the above-mentioned, the blending component should contain a reasonable proportion of saturated light ends. Additionally, the octane number of the blending component should be maximized, topping the weak and exhibiting improved blendability.

Mild hydrocracking allows the aromatics to be almost completely hydrogenated in one reaction step, while producing a certain amount of paraffins over different reaction mechanisms [28]. The resulting saturated compounds have a lower boiling temperature than aromatics of the same carbon number. In addition, there is a further lowering of the boiling temperatures due to the formation of low-molecular cracking products. Noble metals are particularly suitable for the deep aromatic saturation, as they already exhibit high activity at relatively low temperatures and are therefore not limited by thermodynamic equilibrium [29]. To ensure a high octane number, the carrier must be chosen accordingly. Zeolites are beneficial because on the one hand they catalyze ring shrinking and thus isomerization of the naphthenes [30]. On the other hand, shape selectivity can promote the formation of products with high octane numbers [31]. For the critical parameters octane number and boiling curve, ring opening would be another useful reaction step. However, such Pt-zeolite catalysts are not fitting for the ring opening of large methylated aromatics, since the so-called paring reaction leads to a high yield of dealkylation products outside the gasoline boiling range at elevated temperatures and thus carbon loss [32]. At this point, a second reactor, using for example Iridium or Nickel catalysts, seems more promising.

Process and Analytics

For the experiments, a fixed-bed reactor, with an inner diameter of 14.9 mm, was operated top-down in co-current mode. The three commercial catalysts investigated were loaded with 0.3 wt.% platinum and provided pelletized by the manufacturer. Crushed with a mortar, the 100 – 200 µm fraction was diluted with silicon carbide with the same particle size distribution and filled into the reactor between two further layers of pure silicon carbide. Table 2 shows the catalysts used in this work.

TABLE 2. Catalysts as used for the experiments, with a particle size distribution of 100 – 200 µm for both the catalyst and the SiC.

Metal and Zeolite	Metal Loading in wt.%	Catalyst mass in g	Dilution (m_{SiC}/m_{Cat}) in g g⁻¹	Bed height in mm
Pt-HZSM-5	0.3	12.694	6,73	405
Pt-Mordenite	0.3	12.689	8,04	466
Pt-SAPO-11	0.3	20.005	5,01	453

The feed was placed in a storage tank, which was tempered to 50 °C to keep the durene dissolved. To build up the pressure on the liquid side and to convey the heavy gasoline at a flow rate of 0.01 to 5.00 ml min⁻¹, a Bischoff HPD pump – Multitherm 3351 was used and heated to 50 °C. In addition to the liquid phase, the gas was also fed at the top of the reactor. The H₂ was dosed using a Bronkhorst EL-Flow[®] Select MFC and was premixed with the liquid phase, in the approx. first 20 cm of the fixed bed consisting of pure SiC tempered to reaction temperature. The liquid/gas product-mixture was separated in a downstream separator, which had a volume of approx. 800 ml and was operated at ambient temperature. The liquid was extracted via a cooling coil tempered to 0 °C, while also ensuring that no noticeable pressure drop occurred. The gas phase left the separator and was passed on.

The extracted liquid phase was stored gas-tight at below 0 °C and then analyzed in accordance to the parameters specified in DIN EN 228. To measure the composition of the liquid hydrocarbon mixtures, a Reformulyzer M4 from the company PAC and, if necessary, an Agilent GC 7890A calibrated according to the ASTM Standard D6730-01 [33] were used. With the Reformulyzer M4, it was possible to gain an integral insight into the sample by having the instrument differentiate between groups of substances and the number of carbon atoms. In contrast, the GC calibrated to individual components was used as a complementary method, e.g. to determine the content of durene.

The Research Octane Number (RON) was determined according to DIN EN ISO 5164 [34] and the Motor Octane Number (MON) according to DIN EN ISO 5163 [35] by PetroLab in Speyer on a frequently inspected Cooperative Fuel Research (CFR) test engine. Furthermore, octane numbers were determined with a PAC OptiFuel. The method is based on an infrared measurement and a subsequent automated analysis of the spectrum. Since the hydrocarbon

mixtures studied are either very rich in aromatics (feed) or have a high content of naphthenes (products), the underlying model for the OptiFuel was extended as part of the work. The octane numbers measured with the CFR test engine were used as the basis for the new model. A defined number of samples were retained for validation measurements and an error of ± 4 and ± 2 could be determined for the RON and the MON, respectively.

Other important indicators in DIN EN 228 are the so-called E-values. The calculation is based on the boiling curve, which in this work was determined by using a PAC OptiDist following ASTM D86 [36] for large sample volumes and a PAC OptiPMD following ASTM D7345 [37] for small ones. By interpolation between two measuring points, which were recorded with a resolution of 1 vol.%, the E-values could be determined. Furthermore, the vapor pressure was measured with a PAC Herzog HVP 972 using ASTM D6378 [38] at 37.8 °C. The density was determined utilizing a Mettler&Toledo D5 according to a self-developed method at 15 °C.

RESULTS

This work presents if a one-step upgrading process using platinum-supported zeolites is suitable to provide a quality blending component. Table 3 shows the experiments performed for this study as well as the measurement data obtained in accordance with DIN EN 228.

TABLE 3. Experimental data obtained within the hydroprocessing experiments in this study.

Parameters	Pt-Mordenite		Pt-HZSM-5						Pt-SAPO-11			
T _{target} in °C	250	270	230	250	270	290	310	330	270	310	330	350
p in bar	90	90	50	50	50	50	50	60	90	90	90	90
WHSV in h ⁻¹	1.39	1.39	1.39	1.39	1.39	1.39	1.39	1.39	1.39	0.88	0.88	0.88
$\dot{V}_{H_2,N}/\dot{V}_{educt}$ in –	1667	1667	1667	1667	1667	1667	1667	1667	1058	1667	1667	1667
Measurements												
T _{FB,min} in °C	249.1	268.1	228.6	248.4	269.8	290.2	310.1	329.9	270.1	309.0	328.9	348.7
T _{FB,max} in °C	252.8	273.3	234.3	252.8	276.2	294.7	314.9	336.8	277.9	316.0	335.4	355.1
Y _L in wt.%	96.88	91.19	98.98	98.95	97.39	94.51	88.67	78.18	98.01	97.22	97.15	n.a.
RON in –	71.6 ^a	71.9 ^a	n.a.	71.1 ^a	n.a.	71.5 ^a	71.8 ^a	72.2 ^a	n.a.	n.a.	n.a.	n.a.
MON in –	74.3 ^a	75.6 ^a	77.7 ^b	77.3 ^a	78.1 ^b	78.8 ^a	79.6 ^a	80.8 ^a	76.8 ^b	77.2 ^b	77.3 ^b	77.3 ^b
ρ in kg m ⁻³	792.7	772.0	798.6	795.7	790.7	783.0	768.0	748.0	805.6	801.7	799.8	798.4
p _v in kPa	11.0	42.0	2.3	4.8	11.9	24.0	54.0	84.0	1.4	2.8	3.8	3.8
E70 in vol.%	0.0	1.2	0.0	0.0	0.2	0.7	2.5	14.0	0.0	0.0	0.0	0.0
E100 in vol.%	0.4	6.4	0.0	0.0	0.9	3.7	10.5	23.7	0.0	0.0	0.0	0.0
E150 in vol.%	17.0	44.8	2.7	5.8	17.6	29.8	40.0	48.7	0.91	2.0	3.0	4.4
FBP in °C	245.0	215.0	242.0	240.0	240.0	223.3	219.7	208.3	243.0	239.0	241.0	238.0
Aromatics in vol.%	2.7	1.55	2.25	2.13	2.30	2.19	2.02	1.74	2.29	1.67	1.79	2.86
C ₁₀ -aromat. in vol.%	0.19	0.09	0.06	0.11	0.53	0.07	0.18	0.27	0.31	0.09	0.22	0.83
iso-Par. in vol.%	2.02	8.20	0.90	1.50	3.27	4.45	8.20	14.53	0.69	0.76	0.96	1.01
n-Par. in vol.%	0.21	0.74	0.41	0.67	2.95	2.76	4.64	7.96	0.39	0.49	0.56	0.92
Naphthenes in vol.%	95.06	89.48	96.42	95.70	91.41	90.55	85.08	75.71	96.65	97.09	96.68	95.16
Olefines in vol.%	0.01	0.02	0.01	0.00	0.06	0.05	0.05	0.06	0.00	0.01	0.02	0.05

a) Measured with a CFR-Motor; b) Measured with FTIR according to own method

T_{target} describes the target temperature for each experiment, whereby T_{FB,min} and T_{FB,max} are the minimum and maximum temperatures measured in the fixed bed due to the exothermic reaction. The listed pressures were adjusted during the experiment to achieve an almost complete conversion of the aromatics. The Pt-HZSM-5 catalyst exhibited the highest hydrogenation activity. An almost full conversion was already achieved at a pressure of 50 bar, while for the remaining catalysts Pt-SAPO-11 and Pt-Mordenite a pressure up to 90 bar was necessary. Additionally, for the SAPO-11 catalyst, the WHSV had to be reduced from 1.39 to 0.88 h⁻¹ to reach a full conversion at temperatures of 310 °C and higher.

In cracking processes used to produce a fuel fraction, the limiting operating variable is the yield or selectivity towards products in the boiling range of gasoline. The complex reaction network involved in hydrocracking inevitably results in low molecular weight compounds, which consequently reduces the value. The decision in favor of a particular operating point is therefore not solely based on the maximum achievable quality of the product but requires comparing to the gasoline yield. Therefore, the parameters to be optimized are discussed as a function of the gasoline

yield. Figure 1 shows the development of the octane numbers for the different gasoline yields of the investigated catalysts.

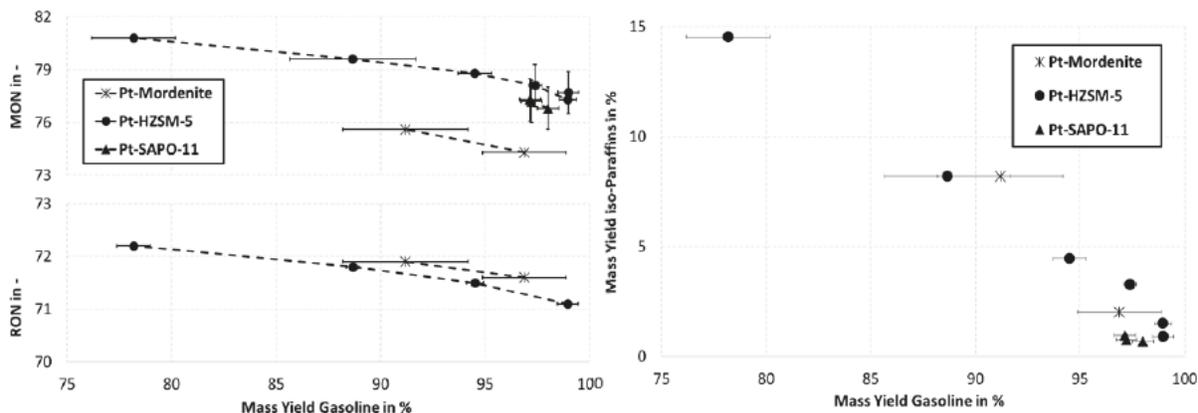


FIGURE 1. RON and MON (left) and mass-yield of paraffins (right) for different gasoline yields. Experiments performed according to the parameters listed in Table 3 utilizing three catalysts.

To evaluate the MON, the data obtained from the CFR motor experiments and the FTIR measurements were used. For the RON measurements, the standard deviation of ± 4 obtained with FTIR was considered too high. Therefore, only the CFR measurements were used and no RON data can be provided for the Pt-SAPO-11 experiments. Throughout the range of parameters investigated, MON always exceeds RON, which is probably caused by the high naphthenic content of the samples. The overall RON and MON values are beneficial because for naphthenes larger than C_9 they are typically <35 and <30 respectively and therefore in a lower range [39]. The MON varies depending on the catalyst used; Pt-Mordenite results in the lowest ones, followed by Pt-SAPO-11 and Pt-HZSM-5. The catalyst-dependent selective isomerization of naphthenes justifies these results. Especially at high gasoline yields between 97 and 100 wt.% hardly any paraffins were formed and the difference must derive from naphthenes.

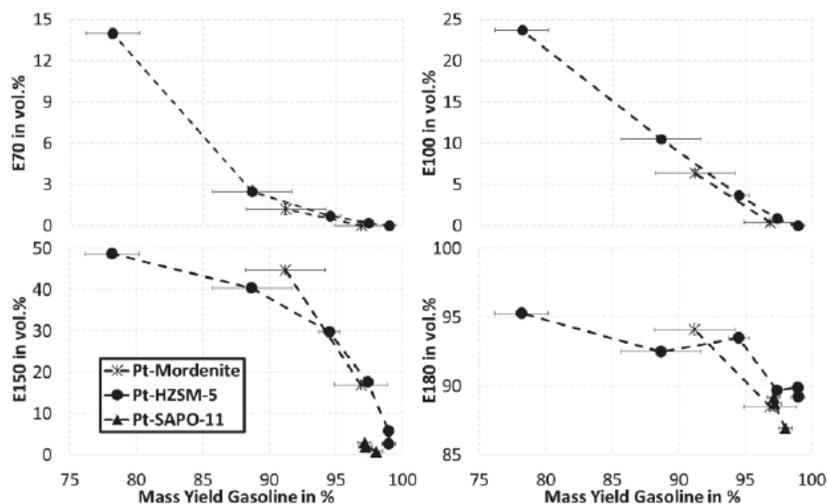


FIGURE 2. E-Values as a function of the mass yield of gasoline. Experiments performed according to the parameters listed in Table 3.

Towards lower gasoline yields, both MON and RON rise, due to the increasing iso-paraffin content. As shown in Fig. 1, the yield of iso-paraffins scales linearly with the gasoline yield. However, an increasing reaction temperature (decreasing gasoline yield) leading to enhanced naphthene isomerization and thus an increased octane number cannot be excluded. In contrast to MON, no dependence on the catalyst is evident for the RON in the studied parameter range. The values obtained by the CFR engine are nearly congruent for Pt-Mordenite and Pt-HZSM-5. Considering the MON-values for Pt-SAPO-11 between the other two investigated catalysts, it can be assumed that the RON-values for Pt-SAPO-11 are comparable with the other two. For both studied octane numbers, especially MON benefits from an

increasing iso-paraffin yield, which is in agreement with results from Santikunporn et al. [31]. While for Pt-HZSM-5 the MON increases by 3.5 between a gasoline yield of 99 and 78 wt.%, the RON only increases by 1.1 in the same range. Compared with DIN EN 228, the measured MON of up to 80 is promising. The RON values of 71 to 72, on the other hand, are too low. Nevertheless, a standard-compliant fuel is possible when blending with the high-octane bioliq[®] gasoline. In addition to maximizing the carbon efficiency of the overall process, the main purpose was to increase the proportion of light ends in the distilled light gasoline by utilizing the upgraded heavy gasoline fraction. Figure 2 illustrates the boiling characteristics defined according to DIN EN 228. The E150 benefits most clearly from cracking, which at a yield of 90 wt.% for Pt-HZSM-5 is almost 40 vol.%. A similarly sharp increase can be observed for Pt-Mordenite. However, only two points were measured. Pt-SAPO-11, on the other hand, shows only a slight cracking activity. A further increase can be seen for the E100, where Pt-HZSM-5 and Pt-Mordenite show almost no difference within error margin. For this parameter, the dependence on the gasoline yield is linear. In the case of Pt-SAPO-11, no production of components in this boiling range was observed. The difference between the bioliq[®] light gasoline and the DIN EN 228 is notably large for E70, which therefore is the most critical value. The proportion of light ends up to 70 °C is just 1.1 vol.% whereas the standard requires at least 22 vol.% (see Table 1). This parameter increases only slowly for low gasoline yields and starts to rise sharply at approximately 88 wt.%. From a process technology perspective, this range is excluded due to the high carbon loss through cracking.

CONCLUSIONS

Three catalysts were investigated for the one-step upgrading of an aromatics-rich heavy gasoline from the bioliq[®] process. Among the investigated catalysts, the Pt-HZSM-5 is performing best for the presented purpose. The achievable octane number was the highest whereas for the yield of light ends there was almost no difference noticeable. In addition the used operating pressure is the mildest for Pt-HZSM-5. Almost a complete hydrogenation of the aromatics was already possible at 50 bar. The optimum gasoline yield is 90 wt.%, at which the E150 and E100 could be increased by almost 40 vol.% and 10 vol.%, respectively. Also, the carbon loss is still in an acceptable range. To further improve the E70, a second ring-opening reaction step could be introduced, in which the rings of the naphthenes are opened to form lower boiling paraffins. Thus, the blendability could be increased further.

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