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Improving the gasoline quality of liquid products from the Fisher–Tropsch process

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ABSTRACT

The un-fractionated, un-hydro treated liquid fractions from the high temperature Fisher–Tropsch (HTFT) process was aromatized over HZSM-5 catalysts at different reaction temperatures and pressures to determine the impact. The flame ionisation detector–gas chromatography (FID–GC) results indicated that there were high amounts of aromatic and BTX (benzene, toluene, and xylenes) compounds contained in the gasoline fraction at a reaction temperature between 400 and 425 °C. Over a period of 6 days of TOL, the estimated Research Octane Numbers (RON) of different streams ranged between 102 and 93 and Motor Octane Numbers (MON) between 92 and 80. The RON and MON values of the streams resulting from the aromatization reaction indicated an improvement in octane and hence improved the blend ability or the component.

1. Introduction

The high temperature Fisher–Tropsch (HTFT) process produces liquid products that are composed of mainly straight chain α-olefins and paraffins in addition to gaseous products. The liquid fraction from the HTFT process contains small amounts of branched, cyclic and aromatic hydrocarbons. Due to the low concentration of the branched, cyclic and aromatic compounds in the HTFT streams, the octane rating is relatively low and upgrading is required. A research study was formulated to investigate the possibility of upgrading the un-fractionated, unhydro treated liquid fraction from the HTFT process using medium pore size zeolites. The main purpose was to produce liquid product fractions that are mainly composed of aromatic compounds that can be more versatile for blending purposes. The medium pore size zeolites have been successfully employed in the petroleum and petrochemical industries to produce unique hydrocarbon materials with high-octane value from different hydrocarbons with low octane value. The HZSM-5 was used in this investigation because of its medium pores that were anticipated to form product fraction mainly in the gasoline range.

1.1. Some general information on the reactions of hydrocarbons over acidic material

Catalytic cracking: Cracking of hydrocarbons can be classified into three categories—mononuclear cracking, bimolecular mechanism and oligomeric cracking [1]. The intermediate species formed from the three mechanism can be in the form of two carbocations, i.e. carbonium and carbenium ions.

Isomerization: Isomerization of olefins in the acidic material may occur via double bond shifting or skeletal isomerization [2]. Alkanes undergo skeletal isomerization. The degree of branching in alkanes and olefins is also restricted by the pore sizes of the acidic materials. Isomerization of C_7 alkanes was found to be slower than cracking and very small amounts of branched C_7 were observed at a temperature of 450 °C and a pressure of 1 bar [2]. At our operation temperature, isomerization of paraffins and olefins is expected to be low as isomerization becomes predominant at lower temperatures over a bifunctional catalyst and in the presence of hydrogen [1].

Aromatization: Aromatization is an important reaction in refinery and petrochemical industries. The well known industrial applications of zeolites in the aromatization process include M-2 forming process proposed by Mobil, Cyclar process jointly developed by BP and UOP and Aroforming process developed by IFP and SALUTEC. The M-2 forming process converts light hydrocarbons to BTX aromatics over a HZSM-5 catalyst [3,4]. Aromatization of olefins is reported to be significant at about 370 °C [3]. The Cyclar process uses a gallium-doped ZSM-5 catalysts to convert light aliphatics such as propane and butane into aromatics [4]. The Aroforming process is designed to aromatize a large range of aliphatic hydrocarbons such as liquefied petroleum gas and light naphthas [4]. The aromatic products formed are reported to be independent of the feed composition and formed in a consecutive reaction pathway via cracking and hydrogen transfer reactions [3].

The mechanism of alkane and paraffin aromatization involves a number of parallel reactions taking place such as cracking,

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oligomerism, cyclisation, isomerization. Formation of aromatics from paraffins and olefins is expected to be accompanied by the production of hydrogen molecules. The hydrogen formed from aromatization as a by-product is often not observed in the product fractions. The main reason is based on the fact that most hydrogen is anticipated to be consumed by carbenium ions to form alkanes.

Other possible reactions: The following reactions were anticipated to take place but number of parameters are expected to limit the extent of reaction. An example is pore size, reaction conditions (temperature and pressure), WHSV, reactant ratio, etc.

Aromatic alkylation: Mobil–Badger process used in the alkylation of benzene with ethylene operates at temperatures ranging from 370 to 420 °C and pressures ranging from 6.8 to 27.2 bar. The process employs medium pore size ZSM-5 catalyst with benzene:ethylene ratio of 5:20 [3,5–7]. The conditions used in our investigations do not favour alkylation of benzene. It is therefore apparent that very little benzene alkylation is anticipated to take place.

Aromatic transalkylation/dipropotionation: ZSM-5 catalyzes the transalkylation of ethyl benzene to form benzene and diethylbenzene [8]. Xylenes transalkylate much slower when compared to ethyl benzene. This is due to the instability of the carbonium ion and the difficulty to cleave methane [8]. An example of dispropotionation is Mobil's toluene disproportionation process. The process is operated at 450 °C and at a pressure of 20–40 atm. At above 450 °C, toluene disproportionate readily over ZSM-5 to give a near equilibrium mixture of benzene and xylenes. The ratio of hydrogen to hydrocarbons is also important in the process [3].

Xylene isomerization: Mobil vapor phase xylene isomerization converts xylenes and ethyl benzene into paraxylene and benzene [3].

1.2. Some factors affecting the activity of zeolites

Molecular trafficking: This concept explains the diffusional changes due to the differences in the sizes of channels. ZSM-5 has differing channel sizes; the sinusoidal channels and linear channels. The smaller channels are accessible to the smaller molecules while the larger channels are accessible to both small and large molecules [3,9,10].

Spatiospecific selectivity or transitional state selectivity: This type of selectivity was first proposed by Csicsery in 1971 when he observed the absence of symmetrical trialkybenzene in the disproportionation products of dialkyl benzene over mordenine [3]. This type of selectivity occurs when the intermediate molecule is larger than the reactant molecules or product molecules [3,9]. The intermediate molecule becomes spatially constrained either by its size or by its orientation [3]. This type of selectivity is independent of catalysts activity and crystal size but depend on the pore diameter and structure of zeolites [3,9]. An example of spatiospecific selectivity was observed in the selective cracking of paraffins in the medium pore size zeolites [3]. n-Hexane and 3-methyl pentane are readily adsorbed by zeolites but hexane crack at a significantly faster rate than 3-methyl pentane [3]. Cracking of 3-methyl pentane requires more space than n-hexane.

2. Experimental

2.1. Catalyst and reaction conditions

HZSM-5 extrudates obtained from Süd Chemie (T-4480 1/16″) were used as received. The HZSM-5 extrudates had a Si/Al ratio of 90. The fixed bed reactor was loaded with 2.0 g (4 ml) of HZSM-5 extrudates. The stabilised light oil (SLO) fraction ($\sim C_5$–C_{15}) from Sasol (Secunda plant) was fed into the reactor at a feed rate of 1.2 ml/(g h). The temperature of the reactor was varied from 375 to 425 °C. The effect of changing the pressure from 1 to 5 bar at different temperatures was also investigated. Different pressures and temperatures were used at separate runs.

2.2. Product analysis

Ampoule technique: The ampoule technique was used to extract gaseous products as well as feed material from the reactor system. Evacuated glass ampoules of volume of 2 ml were used in the extraction of feed and product materials from the reactor. The sample is extracted from the reactor by pushing the capillary part of the evacuated glass ampoule through the pre-pieced septum and through the fork in the septum. The tip of the ampoule was broken and the gas/vapor streams were collected to the ampoule. By means of a portable burner, the protruding ampoule was heated and sealed. The FID–GC technique was used to analyse feed material and products extracted by the ampoule technique from the reactor system. The product spectrum obtained from the different process conditions used in this investigation contained few products that could not be identified by the FID–GC technique during the beginning of the run (less than 10 mass%). However, the amount of the unidentified products increased after 2 days of time on line (TOL) to the approximate maximum amount of 30 mass% of the total product spectrum during the course of the run. The total amounts of BTX aromatic compounds and total aromatic compounds contained in the gasoline fraction were used to monitor the aromatization activity of catalyst at different reaction conditions.

RON/MON modelling: The octane number is a measure of the anti-knock performance of the gasoline fraction, i.e. its ability to resist knocking as it burns in the combustion chamber [11]. There are two laboratory test methods used to measure the octane number of the gasoline. These tests include Research Octane Number (RON) and Motor Octane Number (MON) [11]. The RON correlates best with low speed, mild knocking conditions whereas the MON correlates best with high speed and high temperature knocking conditions [11]. The current South African specification for the unleaded petrol requires a minimum RON of 93 and 95 for the inland and coastal regions respectively. A minimum MON of 83 and 85 is required for the inland and coastal regions respectively.

Determination of octane numbers: The model developed by Sasol Fuel Technology was used to predict the octane values of the product spectrum. Based on the GC–MS characterization, the octane numbers were predicted for the samples. This involved a number of assumptions, such as that the unknown compounds could be normalised, and that only the compounds present at concentrations in excess of 0.05 mass% made a significant contribution to the overall octane numbers of the sample. The RON and MON calculations were based on a non-linear algorithm that takes into account the ON_{clear} of each molecule, as well as its olefinicity [11,12]. The biggest shortcoming of this approach still is the lack of data for ON_{clear} for a large number of the molecules present in the mix. All these data gaps have been filled for the present purpose by estimation and inspection techniques. It is envisaged that these could eventually be deduced in a more scientific manner by consideration of the reduced kinetics of autoignition of each mole.

The octane values of some of the components contained in the gasoline fraction were estimated using known octane values of compounds with similar properties. In addition, components that could not be identified by the FID–GC technique were subtracted from the product fraction and known components were normalised to 100%. This therefore means that for the model to give reasonable results, the amount of products that cannot be identified by the FID–GC must be minimal.

2.3. Assimilation of the data

Gasoline fraction: The area peaks of the different products in the FID–GC were converted into mass percentages. A total amount of 100% was attained when all the mass percentages of products detected by the FID–GC were added together. The gasoline fraction was estimated from the FID–GC results as the total amount of all products in the C_5–C_{12} range. The different amounts of products in the gasoline fraction were expressed as mass percentages in the gasoline fraction. An example is the total amount of aromatic compounds in the gasoline fraction. The total masses of all the aromatic compounds in the gasoline range were added together and divided by the total mass of all the products in the gasoline range and then multiplied by 100.

3. Results and discussion

3.1. The effect of changing temperature on the aromatization behaviour of the catalyst

3.1.1. Gasoline selectivity (C_5–C_{12})

The SLO feed material used in this investigation contained about 98 mass% of the products in the C_5–C_{12} range. The results obtained from the FID–GC analysis indicated less gasoline fraction produced at 425 °C when compared to the results obtained at a temperature of 375 and 400 °C. At 375 °C the gasoline selectivity ranged between 75 and 85 mass% whereas the amount of gasoline produced at 425 °C was as low as approximately 57 mass% (Fig. 1). The gasoline fraction produced at 425 °C ranged between 75 and 57 mass% whereas the amount of gasoline produced at 400 °C ranged between 70 and 85 mass% (Fig. 1). The FID–GC results also indicated large amount of cracked products (C_2–C_4) produced at 425 °C when compared to the runs performed at 375 and 400 °C. In general it is important to minimize the formation of cracked products and maximize the gasoline fraction.

3.1.2. Gasoline quality

Total aromatic compounds in the gasoline fraction: The gasoline fraction was estimated from the FID–GC results as the total amount of all products in the C_5–C_{12} range. Few peaks in the C_{10} to C_{12} region could not be assigned to compounds. The peaks that could not be assigned were assumed to be aromatic compounds. The value of the unknown peaks express in mass% in the gasoline fraction increased with time on line from 2 to 8 mass%.

The SLO feed materials contained about 12 mass% of total aromatic compounds in the gasoline range. At 375 °C about 50 mass% of total aromatic compounds were observed in the gasoline fraction during the first day of TOL (Fig. 2). A similar catalytic behaviour towards the production of total aromatic compounds in the gasoline range was displayed as indicated by the FID–GC results when the reaction temperature was 400 and 425 °C (Fig. 2). The total aromatic compounds contained in the gasoline fraction produced during the first 6 days ranged between 77 and 51 mass% (Fig. 2). These results suggest that the catalyst deactivated over time on line.

The calculated total amount of aromatic compounds contained in the gasoline fraction is not an accurate way of determining the aromatization activity of the catalyst as well as is its deactivation rate. The total amounts of aromatic compounds were constituted by unknown products which were assumed to be aromatic compounds. The amount of the unknown compounds in this investigation increased after 2 or 3 days of time on line from 2 to 8 mass% and resulted in less accurate results. The total amount of BTX compounds was also used to determine the activity of catalyst towards aromatization reactions.

Amount of BTX compounds in the gasoline fraction: The amount of BTX compounds contained in the gasoline fraction is a comparatively accurate way of measuring aromatization activity of the catalyst. The measured amount of BTX compounds does not include any unknown compounds as in the case of total aromatic compounds discussed above. Also, the peaks attributed to BTX compounds are easily identified in the FID–GC spectra. The SLO feed material contained 3 mass% of BTX compounds in the gasoline fraction.

At 375 °C, the amount of BTX compounds was approximately 23 mass% after the first day of TOL (Fig. 3). The FID–GC results also indicated fast deactivation of the catalyst over time on line at a reaction temperature of 375 °C (Fig. 3). Increasing the temperature from 375 to 400 °C almost doubled the amount of BTX compounds produced during the first day of the run (Fig. 3). The FID–GC results obtained during the first day of the run at a temperature of 400 °C indicated the presence of approximately 40 mass% of BTX compounds contained in the gasoline fraction (Fig. 3). However, when the reaction temperature was increased to 425 °C, the amount of BTX compounds contained in the gasoline fraction over time on line was similar to the results obtained at 400 °C (Fig. 3). Considering the amount of gasoline fraction produced at 400 and 425 °C, the total amount of BTX compounds produced at 400 °C is higher than the amount obtained at 425 °C. At 425 °C, less gasoline

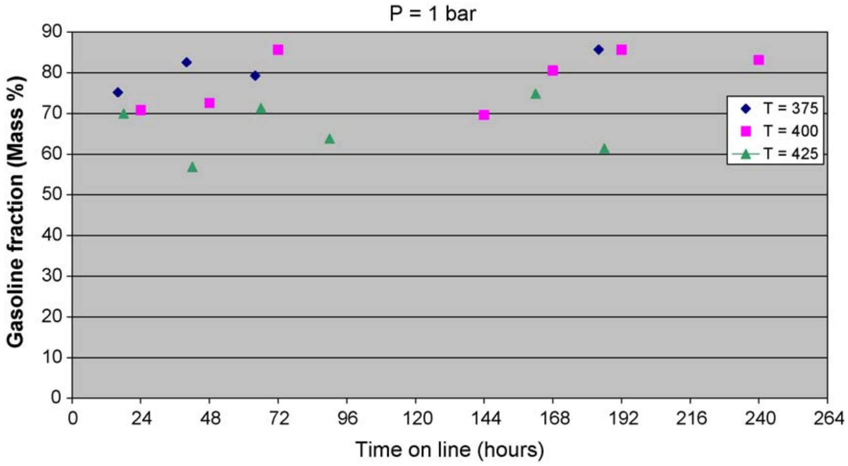

Fig. 1. Gasoline selectivity (C_5–C_{12}) obtained at different reaction temperatures and at a pressure of 1 bar.

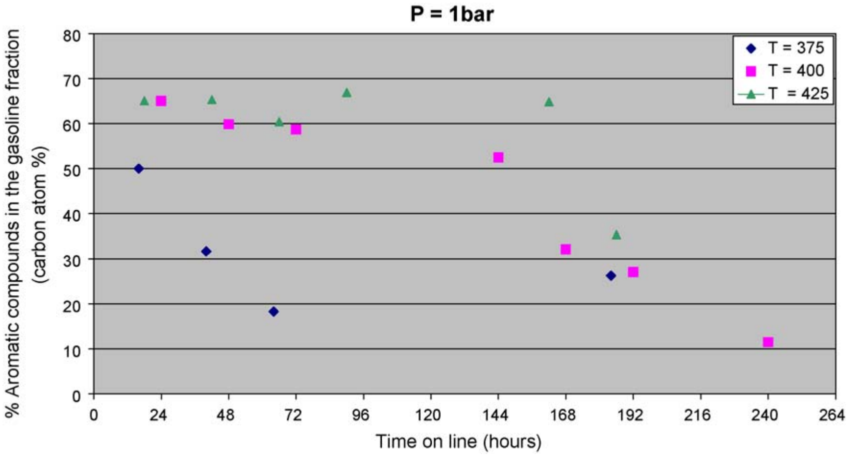

Fig. 2. The amount of aromatic compounds contained in the gasoline fraction at different reaction temperatures and at a pressure of 1 bar.

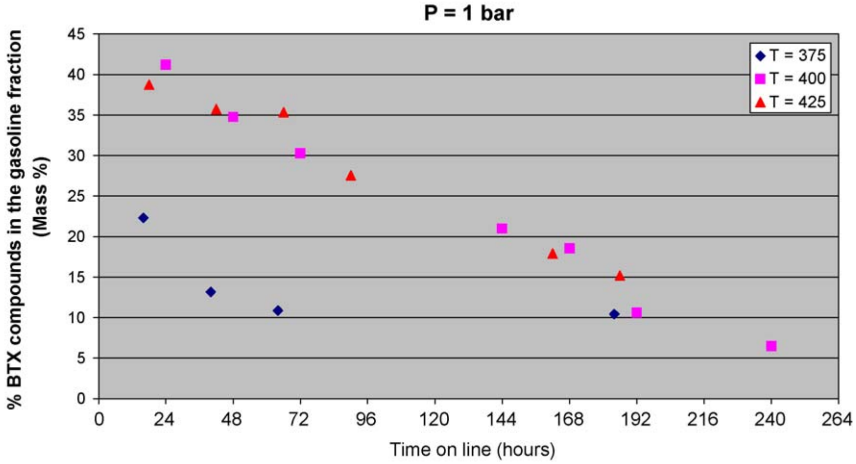

Fig. 3. The amount of BTX compounds contained in the gasoline fraction at a reaction pressure of 1 bar.

fraction was produced and more cracked products were observed when compared to the results obtained at 400 °C (Fig. 3).

The deactivation rate of the catalyst displayed by the total aromatic compounds differs from the deactivation rate displayed by the BTX results (Figs. 2 and 3). The BTX results indicated faster deactivation of the catalysts during the course of the run (Fig. 3). The amount of BTX compounds contained in the gasoline fraction gives a better representative of the activity of catalyst as it does not contain compounds that could not be identified and assumed to be aromatic compounds.

The deactivation of the catalysts could result from pore mouth blockage, blockage of the active sites, blockage on the sinusoidal cavity, etc. The lower deactivation rate observed at higher temperature could be associated to the possibility of decomposing some of the soft coke formed. The decomposition of soft coke at 375 °C is anticipated to be unfavourable and at 425 °C some of the soft coke may be decomposed.

3.1.3. RON/MON determination

The SLO fraction was used as feed material in this investigation and is a product from the HTFT synthesis. The CFR engine test have not been performed on the petrol fraction extracted from the SLO material, this is possibly due to the fact that the fraction contains a large amount of straight chain olefins and paraffins and small amounts of branched chains, cyclic and aromatic compounds. The straight chain hydrocarbons are reported to have low octane numbers and could easily damage the engine.

The octane prediction model developed by Sasol Fuels Technology was used to obtain an approximate octane value of petrol fraction from the SLO material. Results show an approximate RON of 60 and MON of 50 (Fig. 4). As expected, these values are very low when considering the South African petrol specifications. The low octane value results from low amounts of branched, cyclic and aromatic compounds contained in the gasoline fraction of SLO.

RON/MON modelling of the product fraction: FID–GC results obtained from the first day, third day and sixth or seventh or eighth day of the run were modelled in order to get an insight into the quality of petrol. The RON and MON values of the product fraction obtained during the first day of the run are expected to be accurate because the FID–GC technique could identify most of the products in the gasoline range. However, the RON and MON results obtained after 2 days of the run are less accurate as a result of the increase in the amount of the products that cannot be identified by the FID–GC technique and were subtracted from the gasoline fraction.

At 375 °C, the predicted RON and MON values from the petrol fraction obtained during the first day of the run are comparable to the required values for South African petrol (Fig. 4). The highest RON was obtained at reaction temperature of 375 °C was about 94

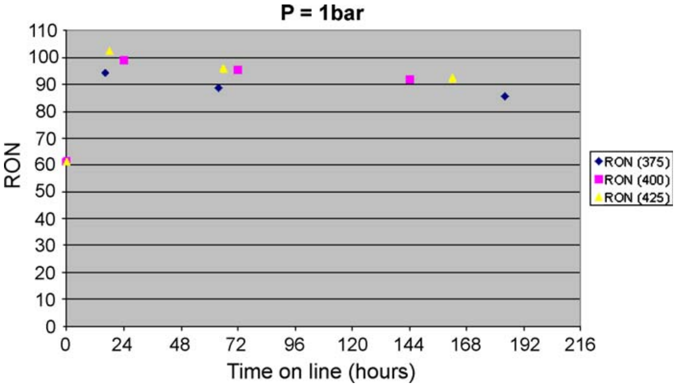

Fig. 4. RON values of gasoline fractions extracted at different times of the run at a reaction pressure of 1 bar.

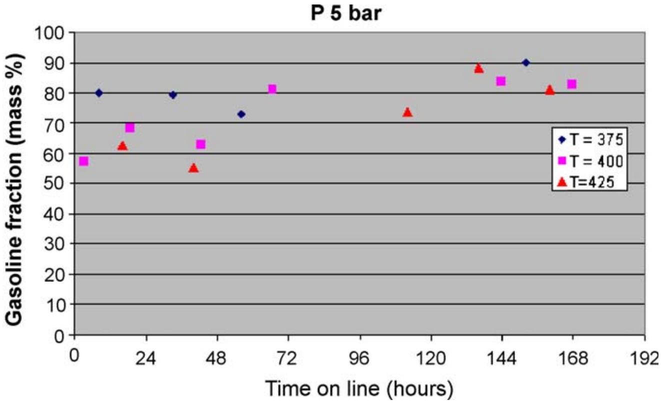

Fig. 5. Gasoline selectivity (C_5–C_{12}) obtained at different reaction temperatures and at a pressure of 5 bar.

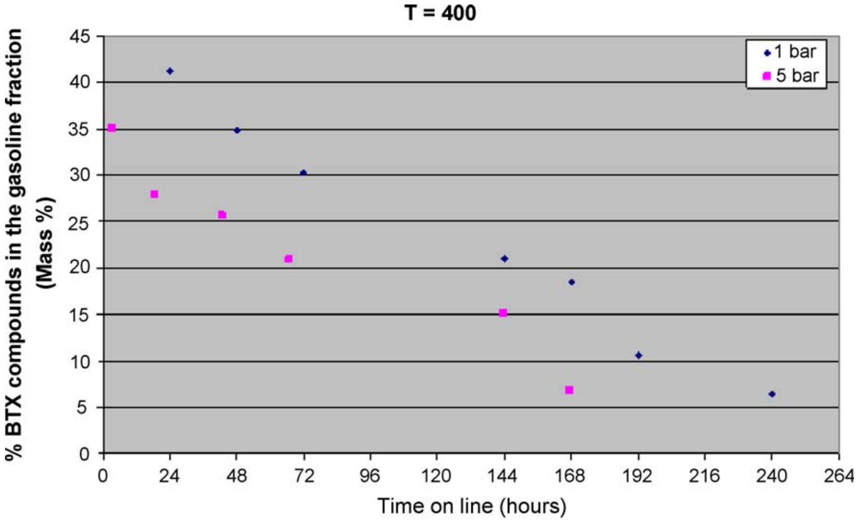

Fig. 6. The effect of pressure in the production of BTX aromatic compounds at the reaction temperature of 400 °C.

with a corresponding MON of 87. The petrol fractions obtained at 400 and 425 °C had higher RON (102–93) and MON (92–80) values (Fig. 4). The petrol fraction obtained at 400 and 425 °C during the first day of the run can be used as good blending components. The higher amounts of aromatic compounds observed at 400 and 425 °C are responsible for the higher RON and MON value. The modelled octane values obtained after the fifth day of the run at different temperatures indicated low octane numbers of the petrol fraction obtained from the different temperatures (Fig. 4).

3.2. *The effect of changing pressure on the aromatization behaviour of catalyst*

3.2.1. *Gasoline selectivity*

A similar trend of the gasoline selectivity results is observed at 5 bar when compared to the results obtained at 1 bar (Figs. 1 and 5). The amount of gasoline fraction produced at 425 °C is less than the amount of gasoline formed at 400 and 375 °C (Fig. 5). The FID–GC results also indicated a lot of cracked products (C_2–C_4) formed at 425 °C accompanied by traces of diesel (C_{13+}) fraction formed.

3.2.2. *Gasoline quality*

BTX aromatic compounds in the gasoline fraction: The BTX compounds produced over time on line at different temperatures were used to evaluate the effect of pressure on the behaviour of catalyst towards aromatization. Increasing the pressure from 1 to 5 bar at an operating temperature of 375 °C did not show any considerable difference in the formation of BTX aromatic compounds after the first day of the run. However, at 400 °C the amounts of BTX formed over time on line at a pressure of 5 bar were lower than the amount formed at 1 bar (Fig. 6). Similar results were obtained at 425 °C; less BTX aromatic compounds were formed at 5 bar when compared to the BTX aromatic compounds formed at 1 bar.

These results suggest that high pressures suppress the formation of BTX aromatic compounds. Considering the thermodynamic aspects, the formation of aromatic compounds from hydrocarbons is expected to be more favourable at lower pressures. Aromatization involves cyclisation accompanied by dehydrogenation. These processes then result in the formation of more product molecules when compared to the reactants hence high reaction pressures are not conducive for the aromatization reactions.

4. Conclusion

The FID–GC results indicated a considerable increase in the amount of aromatic compounds when the temperature of the reaction was increased from 375 to 400 °C and at a pressure of 1 bar. Increasing the temperature from 400 to 425 °C did not show any significant improvement in the performance of the catalyst towards aromatization. An increase in the cracking activity of the HZSM-5 catalyst was also displayed by the FID–GC results when the reaction temperature was 425 °C and lower gasoline selectivity was observed. Increasing the pressure from 1 to 5 bar resulted in lower activity of catalyst towards aromatization.

The catalyst used in the investigation deactivated fast and to improve the process a different catalyst may be employed. The catalyst must be able to sustain activity for a longer period. Different reaction conditions and different rectors may also be employed.

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References

[1] M. Stöcker, Micropor. Mesopor. Mater. 82 (2005) 257.
[2] J.P. Marques, I. Gener, J.M. Lopes, F.R. Ribeiro, M. Guisnet, Catal. Today 107–108 (2005) 726.
[3] Y.N. Chen, W.E. Garwood, F.G. Dwyer, Shape Selective Catalysis in Industrial Applications, Marcel Dekker, New York, 1989.
[4] M. Guisnet, N.S. Gnep, F. Alario, Appl. Catal. 89 (1992) 1.
[5] T.F. Degnan Jr., C.M. Smith, C.R. Venkat, Appl. Catal. 221 (2001) 283.
[6] C. Perego, P. Ingallina, Catal. Today 73 (2002) 3.
[7] J.S. Beck, W.O. Haag, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Wiley-VCH, New York, Handbook of Heterogeneous Catalysis, 1997, pp. 2123.
[8] D.S. Santilli, B.C. Gates, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Wiley-VCH, New York, Handbook of Heterogeneous Catalysis, 1997.
[9] M. Guisnet, J. Gilson, in: G.J. Hutchings (Series Editor) M. Guisnet and J. Gilson (Eds.) Imperial College, London, Zeolites for Cleaner Technology, 2002, pp. 1.
[10] N. Viswanadham, G. Murali Dhar, T.S.R. Prasada Rao, J. Mol. Catal. 125 (1997) 87.
[11] R. Barber, K. Carabell, J. Freel, P. Fuents-Afflick, L. Gibbs, H. Gooch, K. Hoekman, M. Ingham, M. Johnson, D. Kohler, R. Leaper, D. Lesnini, M. Lano, W. Lee, M. Sztenderowicz, S. Welstand, Motor Gasolines Chevron Product Company Technical Review, 1996.
[12] W.E. Stewart, Petrol. Refiner. 38 (1959) 135.