

Gas Condensate Conversion into High Octane Gasoline

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Abstract: Gasoline production has become a great challenge due to stringent standards enforced. The feasibility of zeolite-based catalyst to be used in the reforming process of gas condensate into high octane gasoline was investigated. Reaction under nitrogen rich gas and hydrogen rich gas were carried out. Characterization of the liquid product was carried out to ensure the local and international standard, MS 118 EURO 2M and EN 228 EURO 5, respectively requirement were fulfilled.

Key words: Gasoline, aromatization, gas condensate, zeolite catalyst, liquid product, rich gas

INTRODUCTION

Rapid growing of global demand for liquid fuels where projection to increase to 38% from 87 MMbbl/d in 2010 to 119 MMbbl/d in 2040 of its consumption (Velichkina *et al.*, 2008). Liquid fuels, mainly gasoline has become a great challenge to be produced as stringent regulations by enforcing discontinuation of addition of leaded compounds to boost the octane number in gasoline and reduction of BTX content have lead to the research of alternatives process. European directive has made obligatory for lead content to be <5 ppm in Euro 4, 5 as well as in Euro 6 specifications. Besides that the availability of massive amount of unconventional hydrocarbon gasoline feedstock, e.g., gas condensate, petroleum gas, gas gasoline, etc., have gain increasing interest among researchers/engineers to develop and change the conventional process and/or reformulating gasoline.

Based on US geological survey, new recoveries of reserves have doubled as compared to in 80's. Apparently, 80% of new recoveries of gas reservoirs are smaller than the minimum that make transportation by pipeline as a feasible method. Gudmundsson and Graff (2003) reported that about 40% of the total gas reservoirs are classified as "stranded". The major drawback of "stranded" reserves development is the transport system for construction of long-distance and large-diameter steel pipelines to transfer the gaseous to domestic, commercial and industrial users where markets do exist (Odumugbo, 2010). Currently, pipeline technology is used for distances <1000 km where liquefied natural gas technology is applied for much larger distances. Therefore, alternative technology other than pipeline has to be implemented.

Table 1: Automotive fuel unleaded gasoline EURO 6 (Velichkina *et al.*, 2008)

Parameters	Euro 6 Min.	Max.
Research Octane Number (RON)	95	-
Motor Octane Number (MON)	85	-
Lead content (mg/L)	-	5
Density at 15°C (kg/m ³)	720	775
Sulfur content (mg/kg)	-	10
Manganese content (mg/L)	-	2
Oxidation stability (min)	360	-
Appearance	Clear and bright	
Olefins (% v/v)	-	18
Aromatics (% v/v)	-	35
Benzene (% v/v)	-	1
Oxygen content (% m/m)	-	3.7
Oxygenates content (% v/v)		
Methanol	-	3
Ethanol	-	10
Iso-propyl alcohol	-	12
Iso-butyl alcohol	-	15
Tert-butyl alcohol	-	15
Ethers (>5°C atoms)	-	22
Other oxygenated	-	15

Conventionally, the massive advent of gasoline on the market is obtained from several sequential and parallel refinery processes including direct distillation of crude oil, cracking and reforming (Antos and Aitani, 2004). The finished gasoline must satisfy the requirements including meeting the minimum anti knock properties where the low octane number component of paraffins has to be converted into higher octane number components of isoparaffins or/and aromatic. As shown in Table 1, the limitation of aromatic component will stimulate the altering composition by reducing the aromatic from 42-25% and increase the isoparaffin from 20-45% so that higher octane number can be achieved (Erofeev *et al.*, 2012). Gasoline range hydrocarbon obtained from direct distillation of crude oil from atmospheric column without utilization of any catalyst is known as "straight run". However, the

gasoline yield from straight run is much dependence on the crude oil origins and property which is relatively low (20-25 vol.%) consequently insufficient to cater the demand and profit gain (Antos and Aitani, 2004; Gary *et al.*, 2007). Thus, the longer carbon chain and heavier component has to be further cracked into gasoline range hydrocarbon while the component having low octane number has to be reconstructed in reforming process prior to blending in gasoline pool. According to EIA, statistically 19 gallons of gasoline equivalent to 45 vol.% is produced incorporate the different process routes from one barrel of crude oil for refineries in US.

Research on converting gasoline from gas condensate on zeolite based catalyst has attracted attention for several years. The wide applications of zeolite-based catalyst in petrochemical processes are mainly due to high acidity properties and peculiarity of shape, arrangement and dimension of the channels where the reaction occur are included hydrocarbon cracking, isomerisation, alkylation and hydrogen transfer which makes possible for this objective (Bhatia, 1989). High-octane gasoline production is possible from various hydrocarbon components with boiling point up to 200-250°C. The reactions take place sequentially and parallel on active centers of acid-base zeolite catalyst. The first phase would be the C-C bond scission in paraffins to form unsaturated hydrocarbon followed by hydrogen disproportionation between light paraffins and olefins. Formation of aromatics from the intermediate compounds is then the following stage. Therefore, this research aimed to investigate the feasibility of reforming process using zeolite-based catalyst from low value gas condensate into high-octane gasoline.

MATERIALS AND METHODS

Experimental: A fixed catalyst bed reactor ($V_{cat} = 200$ mL) is used to study the conversion of gas condensate. The reaction temperature was kept constant at 415°C, at feed space velocity of 0.3 h^{-1} , pressure of 22.5 barg with nitrogen and hydrogen flow rate of 10 NI/h. The product stream flowing out from the catalytic reactor made of Hasteloy C22 was sent to a heat exchanger of jacketed pipe where the coolant was domestic water supply, fed into the jacket in a counter current approach. The products discharged from condenser are liquid and gas phase and collected in a high pressure separator. The liquid products composition was determined by gas chromatography, using BP-1 PONA capillary column (100 m×0.25 mm×0.5 m) to evaluate the catalytic activity.

Table 2: Feedstock characterization summary

Tests/Units	Methods	Results
Density@ 15°C (kg/L)	ASTM D 4052	0.7522
Characterization factor	UOP 375	11.7
Total acid number (mgKOH/g)	ASTM D 664	0.02
Nitrogen (mg/kg)	ASTM D 4629	<1.0
Oxygen (wt.%)	GC LOW OX	Not detected (<0.2)
Mercaptan sulphur (mg/kg)	ASTM D 3227	2
Total sulphur (mg/kg)	ASTM D 5453	32
Kinematic viscosity @20C (cSt)	ASTM D 7042	0.728
@40C (cSt)		0.581
Water and sediment (vol.%)	ASTM D 1796	<0.05
Distillation		
Initial boiling point		57.5
5% evaporated		76.0
10% evaporated		80.3
20% evaporated		85.1
30% evaporated		90.4
40% evaporated		96.7
50% evaporated		103.9
60% evaporated		112.5
70% evaporated		123.6
80% evaporated		138.6
90% evaporated		158.8
95% evaporated		173.6
Final boiling point (°C)	ASTM D 86	191.3
DHA		
Paraffins (vol.%)	ASTM D6730	20.3
Isoparaffins		27.9
Olefins		0.7
Napthenes		33.2
Aromatics		16.3
Unknowns		1.5

The octane number was determined using octane meter, calibrated to CFR engine performance. Nickel is commonly used as a promoter in solid catalyst to improve the catalyst activity toward desired product (Velichkina *et al.*, 2007, 2011, 2013; Urzhumova *et al.*, 2011). Thus, because of the high content of Nickel in the reactor material, it is possible that the wall has catalytic effect that would overlay and mislead the result of the catalyst tests. The pre-run experiment is conducted to examine the catalytic affect of the reactor material against the feedstock. The feedstock, gas condensate is pumped into the system without the presence of catalyst. The product obtained is analyzed using GC.

Feedstock characterization: Gas condensate characteristics are significantly depended on its origin. The characteristics will differ in group, fraction composition and physicochemical. Hence, the analysis on the characteristics of gas condensate used as the feedstock is carried out. Table 2 presents the results of the analysis where it is important to note that the feed is mainly consists of hydrocarbon from naphthenes group with (mass %) 33.2, followed by isoparaffins with 27.9, paraffins with 20.3, aromatics with 16.3 and olefins 0.7. The remaining 1.5 vol.% is unknown group of hydrocarbon. The Initial Boiling Point (IBP) of the feedstock is 57.5°C and the Final Boiling Point (FBP) is 191.3°C where the carbon chain range is between

C5-C12. The feedstock has low oxygen and nitrogen content which are <0.2 wt.% and <1.0 mg/kg, respectively with total sulphur of 32 mg/kg and mercaptan sulphur of 2 mg/kg. However, the catalyst used is reported to be insensitive toward sulphur, nitrogen and oxygen-compound. The octane number measured by octane meter which has been calibrated to CFR engine showed that the feedstock has RON 40 which is lower than local and international fuel specifications.

RESULTS AND DISCUSSION

Analysis of the experimental data: The pre-run experiment results proved that there is no catalytic effect of nickel in reactor wall material against the feedstock. The compositions of PIONA in the feedstock (Fig. 1 and 2) are found nearly identical to the product coming out from the reactor without presence of catalyst. The slight differences are resulting from stripping effect of the Nitrogen flow used to keep the system pressure constant. Figure 2 showed the losses of the light components without any additional components formed.

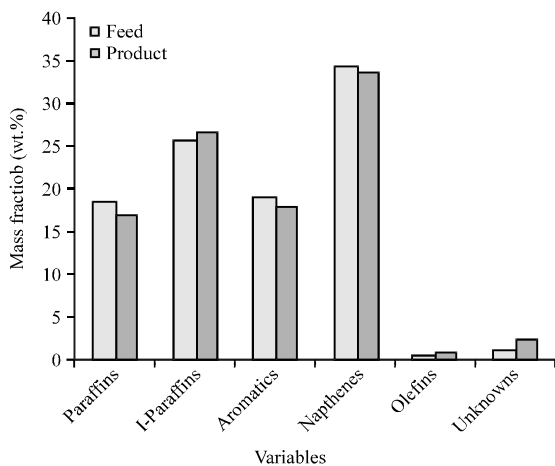


Fig. 1: PIONA analysis of pre-run experiment

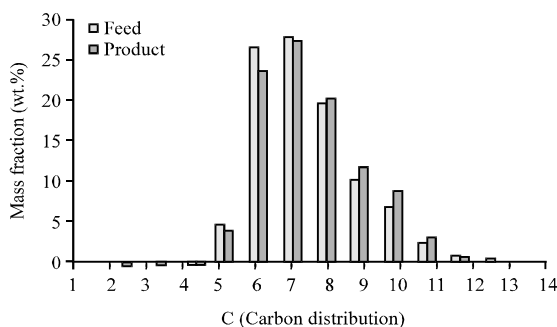


Fig. 2: Carbon distribution analysis of pre-run experiment

The following experimental data are presented in the form of dependencies of the product composition with the presence of hydrogen and nitrogen independently. It is from Fig. 3-4 that with the presence of nitrogen the feed conversion decreases over the time on stream. The catalyst activity declining from RON 109-80 which is 26.4% dropped after 60 h on stream. The highest catalytic activity is attained after 10 h on stream. At the same time, the content of paraffins, isoparaffins and naphthenes increased in the liquid product, leading to the decreasing of octane number significantly. The experimental data shows that the olefin content is approximately constant as olefins is being produced during cracking stage and later being consumed to form aromatics. Corresponded to the research by Rovenskaja and Ostrovski (2003) the observation on olefins contents is similar where the rate of formation and consumption are the same explaining the reaction routes on zeolite-based catalyst. However, a significant amount of light hydrocarbons are formed where the liquid collected is <50% vol. due to cracking and dealkylation reactions occurred. On the other hand, the liquid product yield increased over the time on stream as the catalyst started deactivating and coking formed. With the presence of hydrogen, it was found that the catalyst activity was affected significantly where it provides more stable condition and constant quality of product can be produced. There is no significant change of paraffins, isoparaffins, olefins and naphthenes contents even after >60 h on stream (Fig. 5). As presented in Fig. 6, the octane number is almost constant at RON 106.

The experiments indicate that at both conditions with the presence of hydrogen or nitrogen, the maximum catalytic activity is observed after 10 h of operation. However, the yield increased slightly after 60 h on stream.

Extensive studies showed that gas condensate or straight run cuts conversion over zeolite based catalyst where the octane number improved from 40-60 to 93-97 where the liquid yield ranging from 63-83 wt.% (Stepanov and Ione, 2000, 2005; Stepanov *et al.*, 1992, 1989, 1996). The research finding is supported by another author where the octane number of the gas condensate increased from 65 to 87-97 with liquid yield 50-84 wt.% (Erofeev *et al.*, 2012). Depending on the feedstock composition and operating parameters, the yield of the produced gasoline and the octane number varies from 45-95 wt.% and 67-102, respectively (Erofeev *et al.*, 2012, Velichkina *et al.*, 2008; Urzhumova *et al.*, 2011; Stepanov and Ione, 2000; Stepanov *et al.*, 1996; Vosmerikov *et al.*, 2011; Velichkina *et al.*, 2007, 2013; Velichkina, 2009).

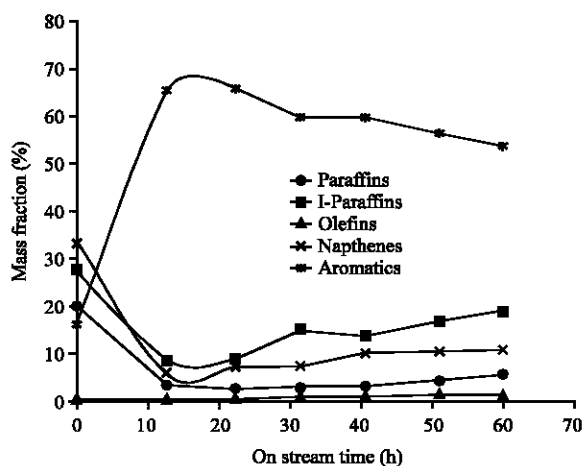


Fig. 3: Conversion of gas condensate at 415°C, 22.5 barg, LHSV 0.3 h⁻¹ with nitrogen 10 NI/h

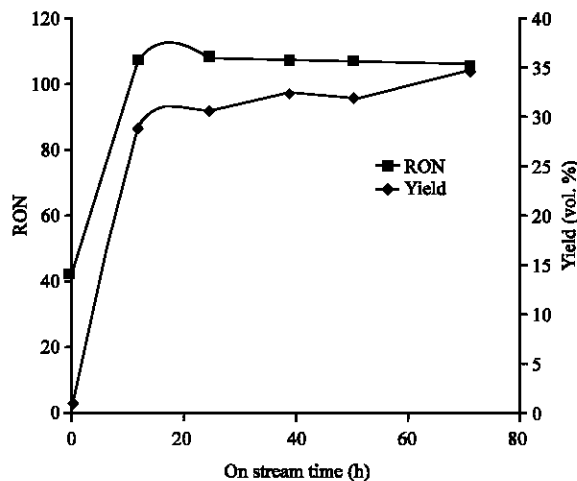


Fig. 6: Octane number and yield with presence of hydrogen

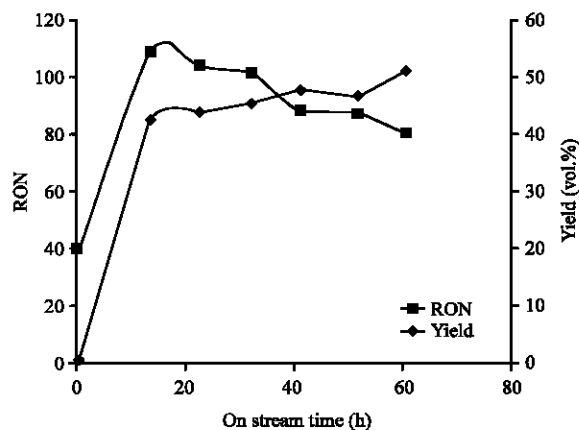


Fig. 4: Octane number and yield with presence of nitrogen

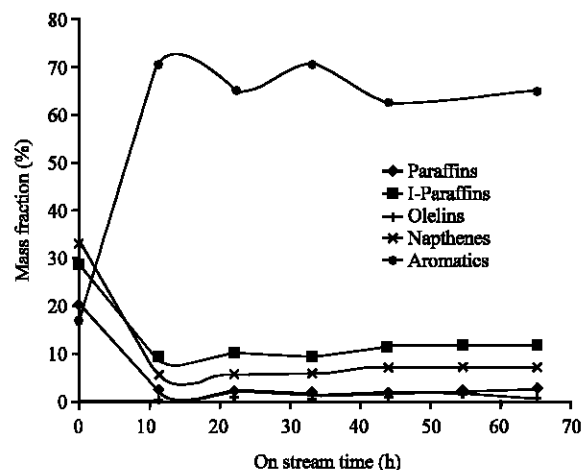


Fig. 5: Conversion of gas condensate at 415°C, 22.5 barg, LHSV 0.3 h⁻¹ with hydrogen 10 NI/h

Zooming into the detail components during the reaction showed that the aromatization reaction has take place over the catalyst. Following the reaction schemes (Rovenskaja and Ostrovski, 2003, 2008) the naphthenic components; cyclohexane and methylcyclohexane are consumed and reformed into aromatic components mainly benzene and/or toluene, 1, 2-dimethylbenzene, 1, 3-dimethylbenzene, 1, 4-dimethylbenzene, respectively. From Fig. 5, the concentration of the aromatic components is higher in hydrogen rich condition as compared to nitrogen.

Simultaneous regeneration might be occurred during the reactions by virtue of hydrogenation of unsaturated hydrocarbon components (oligomer) thus leaving the catalyst activity constantly high as reported by Vosmerikov *et al.* (2011). Report by Vosmerikov *et al.* (2011) confirmed this assumption by thermal analysis data on the spent catalyst operated under hydrogen circulation where lesser amount of coke detected.

The catalytic reactions of zeolite-based catalyst not only reformed the naphthenic gas condensate into gasoline range hydrocarbon which is high in aromatics but simultaneously altered the boiling points of the catalysate. The initial boiling point is much lower than the feedstock and the overall fractional composition increased in both nitrogen and hydrogen conditions. In this case, the liquid product is consists of off fraction since, the local MS 118 EURO 2M and international EN 228 EURO 5 outlined the end boiling point maximum of 215 and 210°C, respectively with the residue is not >2% vol. Table 3 showed the true boiling point of the feedstock and produced gasoline at the maximum catalyst activity; after 12 h of operations. The residue which is >10% vol. will require additional process in order to remove the heavy end products in order to meet the commercial

Table 3: Composition of feedstock and gasoline obtained

Fractional composition (°C)	Gasoline		
	Feedstock	Nitrogen	Hydrogen
IBP	27.8	-11.7	-14.1
10	60.3	80.1	80.1
50	100.9	139.1	139.1
90	164.4	253.7	253.7
FBP	253.7	253.7	253.7

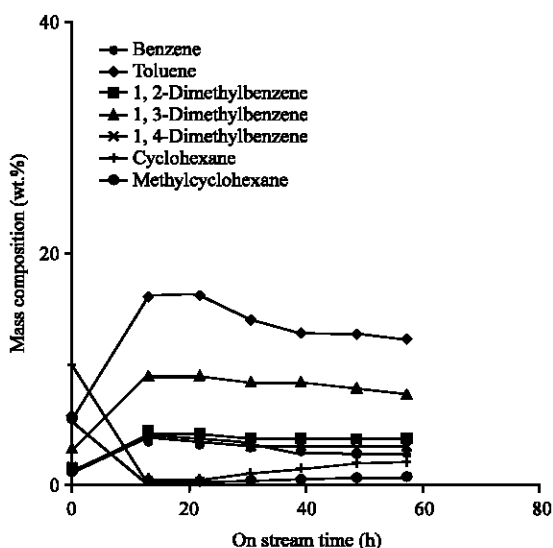


Fig. 7: Conversion of gas condensate at 415°C, 22.5 barg, LHSV 0.3 h⁻¹ with hydrogen 10 NL/h

specification. As a consequence, additional operating cost should be incurred in real application. The same observation is reported by Stepanov *et al.* (1996) where it was concluded that the process conditions will influence the hydrocarbon component produced as well as the boiling point.

However, independent to the formation of heavy ends product, it worth to note that hydrogen does not affect the product composition but helps the stability, activity, reduces intensity of coke formation, prevents the formation of carbon deposition precursor and extends service life of the catalyst as reported by Vosmerikov *et al.* (2011).

In contrast to conventional novel metal-based catalysts, zeolite-based catalyst has advantage due to its resistible properties towards typical catalyst poisons including oxygen, nitrogen, sulfur-containing component, hydrogenous gas or water (Stepanov and Ione, 2000; Velichkina, 2009) (Fig. 7 and 8).

For this reason, the catalyst is insensitive towards such impurities in the feedstock resulting to a need not of pretreatment process. On the other hand, instead of poisoning the catalyst, the sulphur in the feedstock is converted and evolves in the gas phase as H₂S (Stepanov *et al.*, 1996). Table 4 shows the reduction of

Table 4: Impurities in liquid gasoline

Characterizations	Gasoline	
	Nitrogen	Hydrogen
Nitrogen (mg/kg)	<1.0	<1.0
Oxygen (wt.%)	<0.2	<0.2
Total sulphur (mg/kg)	9.0	23.0

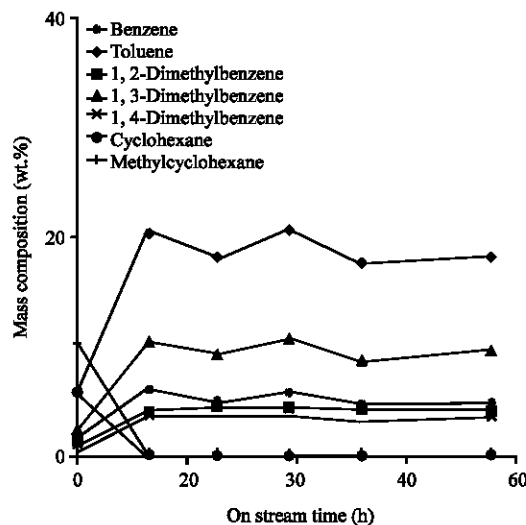


Fig. 8: Octane number and yield with presence of hydrogen

total sulphur content from 32 mg/kg in the feedstock to 9 and 23 mg/kg in both nitrogen and hydrogen environment, respectively. In different study conducted by Stepanov *et al.* (1996) the total sulphur is reduced in range of 95-96 wt.% from the feedstock. From the study conducted, it is concluded that the process temperature will influence the degree of desulphurization reaction where the higher the temperature the greater the reduction.

CONCLUSION

Thus, the data obtained in this research shows that zeolite-based catalyst is able to convert the gas condensate having low octane number into gasoline range hydrocarbon having higher octane number. The presence of hydrogen during the reaction affects the catalyst time on stream but does affect neither product compositions nor catalyst performance. Further research has to be carried out to find the optimum operating condition to maximize the yield of gasoline.

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