Egyptian Journal of Petroleum (2013) 22, 345–350

Egyptian Petroleum Research Institute

Egyptian Journal of Petroleum

www.elsevier.com/locate/egyjp
www.sciencedirect.com

FULL LENGTH ARTICLE

Production of clean gasoline from the condensate

Noureddin Bentahar [a], Said Khelassi [a], Fathy M. Abdelrazek [b,*]

[a] *Department Genius of the Chemical and Pharmaceutical Processes, Faculty of Hydrocarbons and Chemistry, University M'Hamed Bougara – Boumerdes, Algeria*
[b] *Department of Chemistry, Faculty of Science, Cairo University, Giza, Egypt*

Received 29 July 2012; accepted 20 November 2012
Available online 27 November 2013

KEYWORDS

Gasoline;
Algerian condensate;
Algerian bentonite;
Isomerization

Abstract The locally available Algerian bentonite is explored to prepare catalysts for the isomerization of the light fractions of Algerian condensate to produce high quality gasoline of high octane number. Satisfying results are obtained which render these catalysts applicable for a large scale production.

1. Introduction

The progress in the design of the engines, as well as the unceasingly increasing demand for gasoline and the requirements of the quality of the refined products, in particular those related to the environmental protection, made it possible to establish very close links between the characteristics of the fuels and the performance of the engines.

Indeed, last years one can witness non-precedent enthusiasm between the manufacturers and the refiners. Actually, oil industry did not cease formulating and reformulating gasoline grades since the massive advent of car production on the market starting from the gasoline obtained from direct distillation known as "Straight Run".

Two processes are currently used to produce the key components of high octane number; the catalytic reformation and the catalytic cracking. These two processes are complementary and made it possible to obtain gasolines with high octane number, however the composition of these gasolines is strongly aromatic. However, with the growing awakening for the problems of pollution and the environmental protection, the refiners are held to produce a clean gasoline with a much reduced content of aromatics, with a satisfying octane number without chemical additives [1].

The composition of a commercial gasoline generally depends on the refineries and changes from one country to another. Indeed the bases used constituting the gasoline pool can result from various unit operations. These bases or these cuts generally include mixtures of butane, straight run naphtha, isomerized and alkylated hydrocarbons, the reformatted hydrocarbons, FCC gasoline, and the hydro-cracking or coking as well as oxygenated compounds.

Table 1 shows the compositions, expressed as a percentage (in volume), of the gasoline pool in the USA, in Western Europe and in Algeria, according to the American Company Chemical System [2].

One can note in both cases that the significant share returns to the reformatted hydrocarbons and FCC gasoline.

* Corresponding author.
E-mail addresses: nbentahardz@yahoo.fr (N. Bentahar), prof.fmrazek@gmail.com (F.M. Abdelrazek).

Peer review under responsibility of Egyptian Petroleum Research Institute.

Production and hosting by Elsevier

1110-0621 http://dx.doi.org/10.1016/j.ejpe.2013.10.002

Table 1 Constitution of commercial gasoline.

Number	Constituent	USA	Western Europe	Algeria
1	Butane	5.6	5.7	4
2	Light gasoline	4.0	7.6	27
3	Isomerized products	4.7	5.0	
4	Alkylate	13.0	5.9	
5	FCC gasoline	36.2	27.1	
6	Reformatted gasoline	34.7	46.9	69
7	Ethers	1.8	1.8	

Table 2 Properties of isomers.

Constituents	RVP (psi)	Octane numbers		
		RON[a]	MON[b]	(RON + MON)/2
i-Butane	71.90	100.2	97.6	98.9
n-Butane	51.50	95.0	93.5	94.3
i-Pentane	18.93	93.5	89.5	91.5
n-Pentane	14.42	61.7	61.3	61.5
Cyclopentane	9.18	102.3	85.0	93.7
2,2-Dimethylbutane	9.13	94.0	95.5	94.8
2,3-Dimethylbutane	6.85	105.0	104.3	104.7
2-Dimethylpentane	6.27	74.4	74.9	74.7
3-Dimethylpentane	5.65	75.5	76.0	75.8
n-Hexane	4.59	31.0	30.0	30.5
Me-cyclopentane	4.17	96.0	85.0	90.5
Cyclohexane	3.02	84.0	77.2	80.6
Benzene	2.98	120.0	114.8	117.4
C_7 (in the feed)	1.97	55.0	55.0	55.0
C_7 (in the produit)	2.10	82.0	71.0	76.5

[a] Research octane number.
[b] Motor octane number.

Like it was indicated previously, as the demand for octane number grows, the problem arising from the presence of the light fractions of weak octane number makes it difficult to obtain a suitable commercial gasoline.

To compensate, at least partially, the deficiency in octane number it seemed mandatory to produce gasolines rich in iso-paraffins [3]. Thus the process of isomerization of the light fractions contained in particular paraffins (five and six carbon atoms) seemed very useful for the production of a light gasoline base of good quality and of raised octane number due to the anti-knock properties of the iso-paraffins which it contains. Table 2 shows the indices of the octane number and the Reid Vapor Pressure (RVP) of some examples of hydrocarbon isomers [4].

However its contribution to the gasoline pool remains limited because of a high vapor pressure and a much reduced availability compared to the two old processes referred to above.

Algeria is one of the largest gas producer countries in the world. The layer of Hassi-R' mel is one of the largest in the world with physical properties presented in Table 3. The production of gas is accompanied by an annual production of condensate in the order of 15 million tons; what places Algeria among the large producers of condensates. These enormous quantities of condensates produced do not find now any industrial application. However, it is to be announced that a small quantity is added to the crude oil before distillation in the Algerian refineries. The remainder is exported in its raw state. This proves however, that the condensate is of superior quality for the production of fuels than the oil itself. Indeed, the condensate is a slightly colored liquid having general characteristics similar to those of an oil fraction. It is practically free of hydrogen sulfide and has a characteristic bitter

Table 3 Analysis of condensate.

N°	Characteristic	Value
1	Density at 15 °C	0.7238
2	API°	66.64
3	Saybolt color	+13
4	Kinematic viscosity, (cSt) at:	
	0 °C	0.91
	20 °C	0.436
	37.8 °C	0.383
5	Not disorder, °C	−55
6	Refractive index	1.40476
7	Tension reid vapor press. (bars)	0.690
8	Water content (% flight)	0.075
9	Molecular mass	117
10	Not aniline (°C)	63.6
11	Characterization factor	12.46
12	Doctor test	Negative
13	Conradson index, % mass	0.38
14	Calorific value, kcal/kg	11,073

odor. The sulfur content is negligible at the time of the exit from the wells of production, and it accompanies natural gas by Hassi-R' Mel at a rate of 220 grams per cubic meter of gas. However, until the current hour Algerian industry was not interested in utilization of this invaluable raw material; only oil and the gas received a particular and privileged attention of the Algerian industrial policy.

From now on Algeria seeks to develop and explore its condensate. Several projects in this direction were born.

In continuation of a recent work aimed at invention of a metal modified nanoporous catalyst for paraffins hydroconversions [5,6], our aim in this work is to study in an objective way; the possibility of developing Algerian condensates by the catalytic isomerization process of its light fractions in vapor phase, in order to obtain gasoline bases with a raised octane number, by exploring bentonite as an Algerian local available catalyst.

2. Experimental

2.1. Materials and methods

The physicochemical analysis of Algerian condensate showed that it is primarily composed of light fractions with a distillation interval ranging from 30 °C to 280 °C. Moreover, it is free from hetero-atomics and in particular those of high molecular masses.

Condensate analysis is characterized by a high percentage of paraffins and a relatively low content of aromatics, naphthenics and olefins.

The implementation of condensate is carried out on the laboratory scale of refining of the Research and Development Center (RDC) – Algeria.

The results of analysis are presented on the following Table 3.

2.1.1. TBP distillation of condensate (T.B.P: true boiling point)

T.B.P distillation was carried out in a column with 50 mm diameter and a height equivalent to 16 theoretical plates, in accordance with standard A.S.T.M D2892. It was carried out under following conditions:

Under atmospheric pressure for the fractions distilling before 200 °C

Under absolute pressure of 40 mm of Hg for the fractions distilling between 200 and 250 °C.

The results are presented in the Table 4.

In the following, three fractions of this condensate known as SP-60, SP-70 and SP-80 were withdrawn from the condensate to perform the analysis and transformation for being developed (Fig. 1). The physicochemical properties of these three fractions are listed in Table 5, here in below:

These condensate fractions which will be used by us as a load were analyzed by chromatography and their chemical composition is presented in Table 6.

2.1.2. Preparation of the catalysts

To be able to treat these loads, we prepared a type of catalyst starting from local bentonite. Clay, object of this study, was extracted from the place named "Azaghar" located in the area

Table 4 Analysis TBP of condensate.

N°	Temperature °C, at 760 mm Hg	% mass cumulated	% volume cumulated	Density at 15 °C
Gas	20	5.15	6.22	0.5900
1	60	28.81	33.15	0.6410
2	80	34.67	37.07	0.6477
3	90	38.04	41.46	0.6539
4	100	45.36	48.75	0.6631
5	110	49.73	53.06	0.6680
6	120	54.55	57.79	0.6911
7	130	60.66	63.72	0.6952
8	140	64.90	67.80	0.6981
9	150	68.46	71.20	0.7005
10	160	72.73	75.25	0.7033
11	170	77.11	79.35	0.7063
12	180	80.03	82.08	0.7083
13	190	82.40	84.28	0.7099
14	200	85.35	86.99	0.7120
15	210	87.45	88.89	0.7136
16	220	89.60	90.84	0.7152
17	235	92.16	93.14	0.7171
18	250	94.27	95.03	0.7187
19	250+	100	100	0.7238

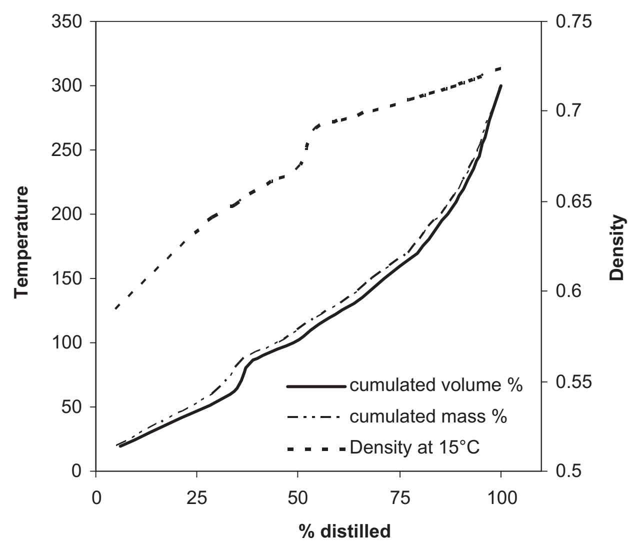

Figure 1 TBP of condensate.

Table 5 Physicochemical properties of the three light fractions of the condensate.

Désignation	Fractions		
	SP[a]-60	SP-70	SP-80
Output compared to the condensate %	29.81	31.74	33.67
Molecular mass	89.5	92.2	95.6
ASTM distillation			
Initial point	32	32	32
10% distilled	37	38	52
50% distilled	40	43	63.5
90% distilled	53	61	72
Final point	60	70	80
% vol distilled	97	97	98
% vol of residue	1	1	0.5
% vol of losses	2	2	1.5

[a] SP: starting point.

Table 6 Chemical composition of loads (fractions).

Components		Charge		
		SP-60	SP-70	SP-80
1	Butane	3.18	2.80	2.16
2	Iso-pentane	4.67	3.50	2.60
3	*n*-Pentane	76.20	60.52	30.20
4	2,2-Dimethyl butane	1.31	1.35	1.40
5	2,3-Dimethyl butane	3.50	2.75	1.80
6	2-Methyl pentane	9.30	10.15	12.65
7	3-Methyl pentane	0	2.75	7.57
8	*n*-Hexane	0	12.42	36.05
9	Cyclopentane	1.57	2.86	3.05
10	Cyclohexane	0.27	0.18	0.14
11	Methyl-cyclopentane	0	0.62	2.20
12	Benzene	0	0.10	0.18
Total		100	100	100
Octane number		67.67	64.17	57.55
Density at 15 °C		0.6410	0.6443	0.6477
Total isomers		18.781	20.50	26.02

Table 8 Composition of 4 catalysts.

Catalyst	1	2	3	4
SiO_2	39.63	49.58	41.28	40.51
Al_2O_3	13.67	16.87	12.83	10.34
Fe_2O_3	6.82	4.03	2.51	2.47
CaO	3.87	2.87	1.97	1.76
MgO	4.36	2.66	1.66	1.63
SO_3	2.46	1.48	0.92	0.91
K_2O	2.67	1.59	0.99	0.97
Na_2O	0.50	1.90	0.17	0.17
Cr_2O_3	0.03	0.02	0.67	4.77
LOI	13.56	8.29	8.88	7.81

of Boghni, Algeria. Its primary treatment was done according to a classic procedure. The bentonite thus obtained is analyzed by fluorescence (XRF) and the obtained results are displayed on following Table 7.

The bentonite thus pre-treated will be used as support for the preparation of a whole of four catalysts differentiated by their chemical composition. These catalysts were prepared according to the following procedure:

The pre-treated bentonite is mixed with the other components such as silica gel, alumina, ammonium chloride and chromium oxide in 1 L of water distilled with 2.5% of ethanol. The mixture is agitated during 8 h at 90 °C; the emulsion thus obtained was filtered off. The cake obtained on the filter paper was transformed into small sticks of length 0.8 cm or 1 cm and 0.2 cm of diameter.

The catalyst thus obtained was left to dry in open air for 12 h; then in an oven (130 °C) for another 12 h after which the temperature was raised to 800 °C for additional 12 h where calcination took place. In this manner four catalysts were developed and their analyses showed the compositions presented on the Table 8 in % mass:

2.1.3. Installation of the system

Three various assemblies were installed at the laboratory to carry out the catalytic isomerization of the prepared loads. The course of the experiments is specific for each installation.

We could note that, the installation whose direction of flow of the load is top to the bottom (see flow chart diagram: Fig. 2) gave better results of isomerization products because the catalytic layer is completely impregnated, therefore completely used. On the other hand, in the other installation, where the direction of flow is upwards, there are preferential sites for the passage of the vapor; therefore the surface of catalysts is not completely exploited.

For the installation designed for isomerization, the tests were carried out at three various temperatures 225 °C, 250 °C and 275 °C, with WWH = 1,4 and the pressure close to the atmospheric pressure as shown in Table 9 *(WWH: weight of the load by the weight of catalyst in one hour).

3. Results and discussion

According to Table 9 above one can see that the outputs of the isomerized products for fraction SP-60 with the catalyst 1 are

Table 7 Analysis results of treated bentonite.

SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	Cr_2O_3	MnO	SO_3	LOI[a]
53.87	18.11	6.67	2.06	3.22	0.50	2.67	0.78	0.18	0.03	0.12	2.46	8.5

[a] Loss on ignition.

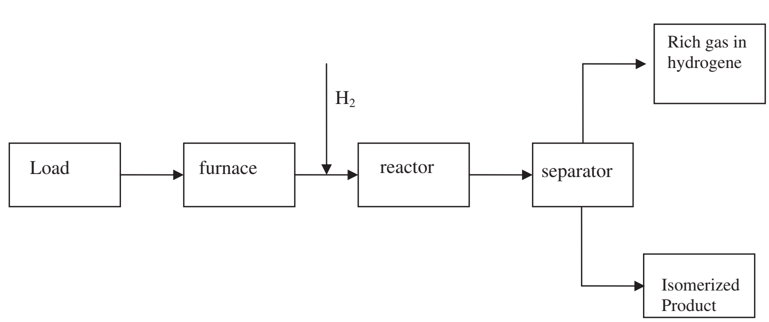

Figure 2 Flow chart diagram of the installation of isomerization.

Table 9 Output of the installation of isomerization.

	Catalyst 1			Catalyst 2			Catalyst 3			Catalyst 4		
Temperature (°C)	225	250	275	225	250	275	225	250	275	225	250	275
Fraction SP-60 output % mass	57.9	59.20	60.0	72.50	79.15	80.83	89.16	91.66	92	80.83	92.50	93.83
Fraction SP-70 output % mass	63.47	67.50	73.61	77.13	82.16	87.53	92.16	93.08	94.17	93.04	94.50	95.32
Fraction SP-80 output % mass	67.46	72.80	75.00	81.66	83.33	85.00	92.50	93.33	95.83	94.16	95.00	96.66

Table 10 Results of some analysis of the isomerized products.

Load of isomerization	Type of catalyst	Temperature of the process	Output	Isomerized products N°	Content of iso-paraffins	Octane number
SP-60	1	225	57.93	1	86.83	89.60
	1	250	59.20	2	86.96	89.70
	1	275	60.00	3	87.15	89.80
	2	225	72.50	4	87.58	89.90
	2	250	79.15	5	87.72	90.00
	2	275	80.83	6	87.75	90.10
	3	225	89.16	7	87.88	90.20
	3	250	91.66	8	87.97	90.30
	3	275	92.00	9	88.35	90.40
	4	225	90.83	10	88.20	90.50
	4	250	92.50	11	88.80	90.60
	4	275	93.33	12	88.79	90.70
SP-70	1	225	63.47	1	87.01	90.10
	1	250	67.50	2	87.32	90.08
	1	275	73.61	3	88.04	91.00
	2	225	77.13	4	88.25	91.50
	2	250	82.16	5	88.78	91.80
	2	275	87.53	6	89.00	92.00
	3	225	92.16	7	89.31	92.60
	3	250	93.08	8	90.95	92.90
	3	275	94.17	9	91.16	93.00
	4	225	93.04	10	91.75	93.20
	4	250	94.50	11	92.01	93.80
	4	275	95.32	12	92.50	94.00
SP-80	1	225	67.46	1	86.50	89.50
	1	250	72.80	2	90.55	89.70
	1	275	75.00	3	90.81	89.90
	2	225	81.66	4	90.92	90.40
	2	250	83.33	5	91.00	90.60
	2	275	85.00	6	91.12	90.70
	3	225	92.50	7	87.21	90.80
	3	250	93.33	8	90.89	90.90
	3	275	95.83	9	91.14	91.00
	4	225	94.16	10	90.74	91.20
	4	250	95.00	11	90.76	91.30
	4	275	96.66	12	91.20	91.50

the lowest, the temperature does not have a significant effect on the outputs. On the other hand for other catalysts, the outputs tend to grow while proceeding to appreciably elevated temperatures. Intermediate results were obtained with regard to fraction SP-70.

The octane number of the obtained isomerization products as for fraction SP-70 is definitely higher than the others (Table 10). For fraction SP-80 the pace of the outputs according to the temperature of the four catalysts is practically the same one, with however an output slightly higher with the catalyst 4. It is the same for the nature of the products of isomerization. Indeed the distribution of hydrocarbons obtained for the two fractions which two fractions (SP-70 and SP-80) shows that in operating conditions, in which the experiments were carried out with the catalyst 4 (containing chromium), showed isomerization products qualities much more marked.

4. Conclusions

In conclusion, we can say that starting from the local natural products, we managed to prepare catalysts containing chromium and alumina enriched bentonite respectively, thus supporting the catalytic isomerization of the light fractions of Algerian condensates. However, it was noted that the best output of the isomerized products is obtained by using catalyst containing chromium and at temperature of 250 °C, and 275 °C at which the octane number is also highest.

As for the choices of the raw material, the experimental results showed that the use of fraction SP-70 is most advantageous.

The convincing results we have obtained encouraged us to check them in a pilot unit before extrapolating them on an industrial scale, this in order to develop exploitation of Algerian condensates.

References

[1] V.E. Emelyanov, S.N. Onojchenco, V.P. Grebenshchikov, Gas condensate gasoline fractions for motor fuel production, Gazovaya Promyslennosti 4 (1993) 24–25.

[2] J.C. Guibet, Carburants et Moteurs, Editions Technip, Paris, 1997.

[3] L.G. Agabelyan, S.N. Khadzhier, N.K.H. Rogovskaya, A.L. Golod, K.G. Ione, V.G. Stepanov, Catalytic transformation of straight-run gas-condensate cuts into high octane-number fuels, Khimya e Technologiya Topliv e Masel 5 (1988) 6–7.

[4] T.H. Russell. Product upgrading: a new opportunity for gas processing. Gas Processors Association (GPA); Annual Convention 68, (1989), 235–240; San Antonio TX USA.

[5] S.S. Muhammed, Synthesis of mesoporous molecular sieves and their use in paraffins hydroconversions, Cairo University, M. Sc. Thesis, 2009.

[6] H.M. Ghobara, M.S. Ghattas, S.S. Muhammed, F.M. Abdelrazek, Synthesis, characterization and catalytic activity of metal modified nanoporous SBA-15, Mansoura J. Chem. 37 (2) (2010) 77–93.