(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
30 March 2017 (30.03.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/051260 A1

(51) International Patent Classification:
B01J 27/16 (2006.01) *B01J 37/00* (2006.01)
B01J 29/06 (2006.01) *B01J 37/02* (2006.01)
B01J 29/40 (2006.01) *C10G 11/05* (2006.01)
B01J 29/48 (2006.01)

(21) International Application Number:
PCT/IB2016/053220

(22) International Filing Date:
1 June 2016 (01.06.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
3600/MUM/2015 22 September 2015 (22.09.2015) IN

(71) Applicant: **HINDUSTAN PETROLEUM CORPORATION LIMITED** [IN/IN]; "Petroleum House", 17, Jamshedji Tata Road, Mumbai, Maharashtra 400020 (IN).

(72) Inventors: **RAVISHANKAR, Raman**; Corporate R&D, Hindustan Petroleum Green Research and Development Center [HPGRDC], KIADB Industrial Area, Tarabahalli, Devanagundi, Hoskote Talkuk, Bengaluru, Karnataka 560067 (IN). **KUKADE, Somnath**; Corporate R&D, Hindustan Petroleum Green Research and Development Center [HPGRDC], KIADB Industrial Area, Tarabahalli, Devanagundi, Hoskote Talkuk, Bengaluru, Karnataka 560067 (IN). **CHALAPATHI RAO, Peddy Venkat**; Corporate R&D, Hindustan Petroleum Green Research and Development Center [HPGRDC], KIADB Industrial Area, Tarabahalli, Devanagundi, Hoskote Talkuk, Bengaluru, Karnataka 560067 (IN). **NETTEM, Venkateswarlu Choudary**; Corporate R&D, Hindustan Petroleum Green Research and Development Center [HPGRDC], KIADB Industrial Area, Tarabahalli, Devanagundi, Hoskote Talkuk, Bengaluru, Karnataka 560067 (IN).

(74) Agent: **DEWAN, Mohan**; R.k.dewan & Co., Podar Chambers, S.a.brelvi Road, Fort, Mumbai, Maharashtra 400001 (IN).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to the identity of the inventor (Rule 4.17(i))*

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

WO 2017/051260 A1

(54) Title: AN ADDITIVE AND A CATALYST COMPOSITION COMPRISING THE ADDITIVE FOR FCC PROCESS

(57) Abstract: The present disclosure relates to an additive and a catalyst composition for a catalytic cracking process of vacuum gas oil for preparing cracked run naphtha having reduced liquid olefin content, and increased propylene and butylene yields in the LPG fraction. The process makes use of a catalyst composition which is a mixture of an FCC equilibrated catalyst and an additive comprising a zeolite, phosphorus and a combination of metal promoters. The process is successful in achieving high propylene and butylene yields in the LPG fraction along with a lower liquid olefin content and increased aromatic content with increase in RON unit in the resultant cracked run naphtha, as compared to that achieved using an FCC equilibrated catalyst alone.

AN ADDITIVE AND A CATALYST COMPOSITION COMPRISING THE ADDITIVE FOR FCC PROCESS

FIELD

The present disclosure relates to an additive for a catalyst composition for a fluid catalytic cracking process.

DEFINATION

As used in the present disclosure, the following word/phrase is generally intended to have the meaning as set forth below, except to the extent that the context in which it is used indicates otherwise.

FCC EQUILIBRATED CATALYST (ECAT): ECAT is a "used/spent" catalyst, containing at least some of the catalyst charged originally. ECAT is used in the petroleum refining industry to convert crude oil fractions into smaller molecular weight hydrocarbon compounds.

BACKGROUND

Vacuum distillation of crude oil results in a variety of petroleum products with a wide range of molecular weights. The heavier hydrocarbon fractions, usually, the left-overs from the vacuum distillation process are converted and refined into more valuable lower molecular weight hydrocarbons with the help of a fluid catalytic cracking (FCC) unit. The ever-increasing demand for gasoline has seen a surge in such refining units.

Vacuum Gas Oil (VGO), a component of the heavier hydrocarbons, is subjected to cracking in an FCC unit, resulting in cracked run naphtha (CRN), fuel oil and offgas as the end-products. The cracked run naphtha (CRN) produced by the cracking of VGO, typically, contains around 45 % to 55 % liquid olefins. When these liquid olefins come in contact with dissolved oxygen, they form hydro peroxides as immediate products, which undergo further reactions to form insoluble oxidized species. These oxidized species that include peroxides, aldehydes, acids, ketones as well as components with molecular weights 200 to 600 g/mol are commonly referred to as gum. This insoluble gum formation in the interior of the process units results in fouling. Although, rigorous exclusion of oxygen or the addition of anti-oxidants are enough to eliminate fouling, in some industrial situations oxygen ingress cannot

be easily prevented. If the liquid olefin content in the CRN is brought down, the gum formation and hence, fouling can be controlled.

Also, the demand for propylene is more as compared to the other cracked products. Various attempts have been made to increase the yield of propylene during cracking. Attempts have been made in the past to improve both the FCC process and the catalyst used in the FCC process. Though, an increase in the propylene yield was observed, the amount of propylene obtained was still low (typically less than 6 %).

Thus, there is a felt need to increase the propylene yield and reduce the liquid olefin content simultaneously in a fluid catalytic cracking process.

OBJECTS

Some of the objects of the present disclosure, which at least one embodiment herein satisfies, are as follows.

It is an object of the present disclosure to ameliorate one or more problems of the prior art or to at least provide a useful alternative.

An object of the present disclosure is to provide an additive for a catalyst composition for a fluid catalytic cracking process.

Another object of the present disclosure is to provide a catalyst composition for a fluid catalytic cracking process.

Still another object of the present disclosure is to provide a fluid catalytic cracking process.

Yet another object of the present disclosure is to provide a fluid catalytic cracking process to obtain a product having an increased propylene yield, an increased butylene yield, reduced liquid olefin content and reduced coke content.

Other objects and advantages of the present disclosure will be more apparent from the following description, which is not intended to limit the scope of the present disclosure.

SUMMARY

In accordance with an aspect of the present disclosure there is provided an additive for a catalyst composition for a fluid catalytic cracking process. The additive comprises a zeolite

impregnated with phosphorus in the range of 10 wt% to 15 wt% with respect to the weight of the zeolite and a mixture of metal promoters comprising zirconium, molybdenum, nickel, cobalt, zinc and gallium, independently in the range of 0.1 wt% to 1.0 wt% with respect to the weight of the zeolite. The "Phosphorus" promoted zeolite is spray-dried and the formulation is loaded with the metal promoters.

A catalyst composition comprising an FCC equilibrated catalyst (ECAT) in the range of 80 wt% to 99 wt% and an additive in the range of 1 wt% to 20 wt%, for a fluid catalytic cracking process is also provided in the present disclosure.

The present disclosure further provides a fluid catalytic cracking process for obtaining a product having increased propylene yield, increased butylene yield, decreased liquid olefin content and reduced coke content, using a catalyst composition. The catalyst composition comprises an FCC equilibrated catalyst (ECAT) and an additive.

DETAILED DESCRIPTION

The present disclosure will now be described with reference to the accompanying embodiments which do not limit the scope and ambit of the disclosure. The description provided is purely by way of example and illustration.

The embodiments herein and the various features and advantageous details thereof are explained with reference to the non-limiting embodiments in the following description. Descriptions of well-known components and processing techniques are omitted so as to not unnecessarily obscure the embodiments herein. The examples used herein are intended merely to facilitate an understanding of ways in which the embodiments herein may be practiced and to further enable those of skill in the art to practice the embodiments herein. Accordingly, the examples should not be construed as limiting the scope of the embodiments herein.

The present disclosure in an aspect relates to an additive for a catalyst composition for a fluid catalytic cracking process. The additive comprises a zeolite impregnated with phosphorus in the range of 10 wt% to 15wt% with respect to the weight of the zeolite and a mixture of metal promoters comprising zirconium, molybdenum, nickel, cobalt, zinc and gallium, independently in the range of 0.1 wt% to 1.0 wt% with respect to the weight of the zeolite.

In an exemplary embodiment of the present disclosure, the amount of the phosphorous in the zeolite is 12 wt%, with respect to the weight of the zeolite.

The precursor of phosphorus is at least one selected from the group consisting of phosphoric acid, phosphates, phosphorous acid, phosphites, pyrophosphoric acid, pyrophosphates, polymeric phosphoric acid, polyphosphates, metaphosphoric acid and metaphosphates.

In an exemplary embodiment of the present disclosure, the amount of the metal promoters with respect to the weight of the zeolite are: 0.5 wt% zirconium, 0.5 wt% molybdenum, 0.5 wt% nickel, 0.5 wt% cobalt, 1 wt% zinc and 1 wt% gallium.

In accordance with the embodiments of the present disclosure, the precursor for each of the metal promoter is a salt of the metal. In an exemplary embodiment of the present disclosure, the precursor of the metal promoter is a nitrate salt of the metal.

The zeolite is at least one selected from the group consisting of ZSM-5, ZSM-11, ZSM-12, ZSM-48, ZSM-57, SAPO-5, SAPO-11, SAPO-17, SAPO-18, SAPO-34, SAPO-44, MCM-22, ZSM-Y and zeolite-beta.

The present disclosure, in an embodiment provides a catalyst composition for a fluid catalytic cracking process. The catalyst composition comprises an FCC equilibrated catalyst (ECAT) and an additive as described hereinabove.

In accordance with the embodiments of the present disclosure, the FCC equilibrated catalyst (ECAT) is present in the range of 80 wt% to 99 wt% of the catalyst and the additive is present in the range of 1 wt% to 20 wt% of the catalyst composition.

In an exemplary embodiment, the FCC equilibrated catalyst (ECAT) and the additive are present in the ratio of 93:7 wt%. In another exemplary embodiment, the FCC equilibrated catalyst (ECAT) and the additive are present in the ratio of 85:15 wt%.

The catalyst composition is used for a fluid catalytic cracking (FCC) process for obtaining a product having an increased propylene yield, increased butylene yield, reduced liquid olefin content and reduced coke content. In the conventional catalytic cracking process, while processing a vacuum gas oil feedstock an FCC equilibrated catalyst (ECAT) is used which yields propylene, typically, less than 6 % and the resultant cracked run naphtha has significant liquid olefin content. In particular, the present disclosure relates to a process that

makes use of an additive in combination with an FCC equilibrated catalyst (ECAT), the mixture thereof increases the propylene yield above 7%, increases the butylene yield and reduces the liquid olefin content.

In an embodiment of the present disclosure, an FCC process for obtaining a resultant product having a propylene yield in the range of 7 % to 16 %, butylene yield in the range of 8 % to 10 %, liquid olefin content in the range of 10 % to 45 % and coke content in the range of 2 % to 7 %, from vacuum gas oil, is disclosed. The catalytic reactor, i.e., a fixed fluid bed micro reactor unit (ACE unit) is supplied by M/s Kayser Technologies, Inc, Houston, USA.

The cracking reactions are carried in the temperature range of 400 °C to 700 °C and at a pressure ranging from 1 atm to 2 atm. In an exemplary embodiment, the reactor is maintained at 530 °C and 1 atm pressure.

The feedstock is vacuum gas oil (VGO) obtained as a left-over from the vacuum distillation of crude oil. An inert gas, a non-limiting example of which is nitrogen, is selected as a carrier gas. The VGO is contacted with a catalyst composition comprising an FCC equilibrated catalyst (ECAT) and an additive comprising a zeolite impregnated with phosphorus and metal promoters comprising a combination of zirconium, molybdenum, nickel, cobalt, zinc and gallium independently in the range of 0.1 wt% to 1.0 wt% with respect to the weight of the zeolite.

The resultant product obtained has a propylene yield in the range of 7 % to 16 %, butylene in the range of 8 % to 10 %, liquid olefinic content in the range of 10 % to 45 % and coke content in the range of 2 to 7 %.

The present disclosure is further described in light of the following experiments which are set forth for illustration purpose only and not to be construed for limiting the scope of the disclosure. The following laboratory scale examples performed in the ACE-MAT testing unit can be scaled up to industrial/commercial scale.

EXAMPLES

Catalytic cracking experiments were carried out in a fixed fluid bed micro reactor unit (ACE unit) supplied by M/s Kayser Technologies, Inc, Houston, USA. The cracking reactions were performed at a temperature of 530 °C and at a pressure of 1 atm and a constant injection time of 30 seconds. The catalyst/vacuum-gas-oil ratio was varied from 3 to 6 wt/wt.

The gaseous products were analyzed using Inficon 3000 micro-GC & Liquid products were analyzed by ASTM 2887 in LT SIMDIS supplied by AC Analytical Controls. The liquid products considered were Gasoline (C5 at 221 °C), LCO (from 221-370 °C) & Bottoms (above 370 °C). Prefrac-PIONA analysis of the liquid samples was carried out using PIONA analyzer and PAC instruments.

The conversion was calculated as the sum of the yields of dry gas, LPG, Gasoline and coke.

Catalyst:

The base catalyst used in the cracking reactions was commercial FCC equilibrated catalyst (ECAT). Additives of the present disclosure were studied at 7 wt% and 15 wt% with the base ECAT. The typical equilibrated catalyst ECAT properties are listed in **Table-1**.

Table-1: Properties of commercial equilibrated catalyst (ECAT)

Attribute	FCC ECAT
Physical Analysis	
Surface area, m^2/g	135
Pore volume (PV), cc/g	0.31
Zeolite surface area (ZSA), m^2/g	74
Matrix surface area (MSA), m^2/g	61
% Crystallinity	11.4
Metals, ppm	
Ni	2000
V	1350
Na	0.29
Fe	0.28
Sb	180
Chemical Analysis, wt%	
Rare earth, wt%	1.75
Al_2O_3, wt%	52.1
P_2O_5, wt%	0.43

Feedstock:

The feed used in the present disclosure was vacuum gas oil (VGO). The detail properties of the feed are listed in **Table-2**.

Table-2: Properties of the feedstock

Properties	VGO
Density at 15°C, g/cc	0.915
Sulphur, wt%	2.0
CCR, wt%	0.60
Pour point, °C	45
Kinematic viscosity @100°C, cSt	7.742
ASTM-7169 Distillation, wt%	
Initial Boiling Point (IBP)	283
5	345
10	365
30	404
50	429
70	457
90	506
95	529
Metals, ppm	
Ni	1.0
V	0.9
Na	1.05
Fe	1.35
SARA, wt%	
Saturates	57.1
Aromatics	33.3
Resins	9.4
Asphaltenes	0.2

Preparation of the additive and the catalyst of the present disclosure:

ZSM-5 with a SiO_2/Al_2O_3 mole ratio of 23 was used as the zeolite for the additive.

10 g of ZSM-5 sample was mixed with varying quantities of ortho phosphoric acid solution and a metal salt solution, especially, a metal nitrate solution to form slurry. The resultant slurry was agitated thoroughly at 25 °C for 3 hours for allowing phosphorus and the metals to

impregnate the zeolite followed by heating in a rotary evaporator maintained at 75 °C under vacuum to obtain a dried mass. The dried mass was calcined at 550 °C for 5 hours and finally ground to obtain an additive powder.

The additive powder was mixed with binder/matrix such as alumina (such as hydrated alumina, gamma alumina, alpha alumina, and psuedoboehmite), fillers such as clay (bentonite, saponite, montmorillonite, kaolin, smectite, etc.). The ratio of active zeolite component: Binder/matrix: filler is: 40: 50: 10 (wt %). The additive powder, binder/matrix and filler were mixed in water to obtain a slurry. The slurry was spray dried to obtain particles having a size of 100 micrometers. The spray dried particles were then calcined at 600 °C for 5 hours to obtain the additive of the present disclosure which is used in the FCC process.

The final catalyst additive formulation contained the metal promoters in both zeolite and binder/matrix. Thus, the whole formulation was active in the FCC cracking process producing higher propylene content and lower olefins content in the resultant product.

FCC ECAT was mixed with this additive powder in ratios ranging from 80:20 to 99:1 wt% and was used as catalyst.

In case of a mixture of metals, all the metal salts were weighed accordingly and dissolved in a required amount of water .

The additives were loaded with phosphorus and metal promoters, according to the following **Table-3**

Table-3 – Metal loading on ZSM-5

Promoter name	"P" Loading with respect to total zeolite content	Metal Promoter Loading on zeolite
MM1	12 %	0.5% Zr, 0.5% Mo, 0.5% Ni, 0.5% Co, 1% Zn and 1% Ga

EXAMPLE 1: Catalytic Cracking with FCC ECAT (comparative example)

Catalytic cracking of VGO was carried out with 100 % FCC ECAT at a reactor temperature of 530 °C, constant injection time of 30 seconds and catalyst/vacuum-gas-oil ratios of 3.0, 3.9, 4.8 and 6 wt/wt. Propylene yield obtained using ECAT is in the range of 6 to 7 wt% for a varying catalyst/vacuum-gas-oil ratio. Table 4 gives the composition of the resultant cracked run naphtha obtained.

Table 4 – Product composition from Example 1

Catalyst	**ECAT**			
Feed	**VGO**			
Cracking Temperature, °C	530.0	530.0	530.0	530.0
Catalyst to vacuum-gas-oil ratio, wt/wt	3.00	3.90	4.80	6.00
Conversion, wt%	69.73	73.18	75.56	77.93
YIELDS, wt%:				
Coke	3.39	4.40	5.05	6.48
Dry Gas (H_2, C_1-C_2)	2.60	2.90	3.16	3.50
LPG	19.29	21.19	21.96	23.33
Propylene	6.13	6.55	6.66	6.87
Butylenes	7.28	7.42	7.30	6.98
Gasoline (C_5-216 °C)	44.45	44.68	45.39	44.62
LCO (216-370 °C)	19.23	18.32	16.83	15.52
Unconverted (above 370 °C)	10.80	8.73	7.61	6.55
% Liq. Olefins	32.00	27.00	25.00	20.02
% Reduction of liq. Olefins	0	0	0	0
% Aromatics	32.89	37.49	39.65	45.79
% Increase in Aromatics	0	0	0	0
RON	94.9	96.1	97.2	98.4
Increase in RON Units	0	0	0	0

Example 2: Catalytic Cracking with 93 % FCC ECAT + 7 % MM1 Additive

The catalyst of Example 2 comprised 7 wt% MM1 additive with 93 wt% FCC ECAT. Catalytic cracking reactions of VGO at reactor temperature of 530 ^{o}C, constant injection time of 30 seconds and cat/vacuum-gas-oil ratios of 3.0, 3.9, 4.8 and 6 wt/wt are studied to see the effect. Propylene and liquid olefin content are shown in Table 5. Increase in LPG yield (Δ LPG) obtained compared to Example-1 was 8.7 wt% to 9.8 wt%.

Table 5 – Product composition from Example

Catalyst	**ECAT + MM1 additive (93 wt% + 7 wt %)**			
Feed	**VGO**			
Cracking Temperature, °C	530.0	530.0	530.0	530.0
Catalyst to Vacuum-Gas-Oil ratio, wt/wt	3.00	3.90	4.80	6.00
Conversion, wt%	68.83	72.67	73.86	77.07
YIELDS, wt%:				
Coke	3.43	4.28	5.22	6.81
Dry Gas (H_2, C_1-C_2)	3.63	4.14	4.53	4.94
LPG	26.13	28.38	29.68	31.10
Propylene	9.55	10.04	10.29	10.65
Butylenes	8.86	8.94	8.60	8.07
Gasoline (C_5-216 °C)	35.64	35.87	34.42	34.21
LCO (216-370 °C)	19.95	18.27	17.70	15.77
Unconverted (above 370 °C)	11.22	9.06	8.44	7.17
% Liquid Olefins	29.88	26.80	19.67	14.81
% Reduction of liq. Olefins	6.63	0.74	21.32	26.02
% Aromatics	40.41	48.68	56.35	61.3
% Increase in Aromatics	22.864	29.848	42.119	33.872
RON	96.6	97.3	102.5	103.5
Increase in RON Units	1.700	1.200	5.300	5.100

Table 5 shows that the propylene yield has increased and is in the range of 9.55 wt% to 10.65 wt%, butylene yields have increased and is in the range of 8.07 wt% to 8.94 wt% and liquid olefin content has decreased (reduction by 6.625% to 26.024%) for all the Catalyst to Vacuum-Gas-Oil ratios as compared to the products of Example 1. At a higher Catalyst to Vacuum-Gas-Oil ratio, the liquid olefin content has decreased significantly. A decrease in the coke yield is also observed when the cat/oil ratio is 3.90. An increase in the Aromatics yields and increase in RON units (1.2 units to 5.3 units) is also clearly observed.

Example 3: Catalytic Cracking with 85 wt% FCC ECAT + 15 wt% MM1 Additive

The catalyst of Example 3 comprised 15 wt% MM1 additive with 85 wt% FCC ECAT. Catalytic cracking reactions of VGO at reactor temperature of 530 °C, constant injection time of 30 seconds and cat/vacuum-gas-oil ratios of 3.0, 3.9, 4.8 and 6 wt/wt are studied to see the effect. Propylene yield obtained with 15 wt% additive in ECAT is in the range of 10.5 wt% to 11.8 wt%. ΔLPG obtained as compared to Example-1 is in the range of 8.7 wt% to 9.8 wt%. Propylene and liquid olefin content are shown in Table 6.

Table 6 – Product composition from Example 3

Catalyst	**ECAT + MM1 additive (85 wt% + 15 wt%)**			
Feed	**VGO**			
Cracking Temperature, °C	530.0	530.0	530.0	530.0
Catalyst-to vacuum-gas-oil, wt/wt	3.00	3.90	4.80	6.00
Conv., wt%	67.41	73.11	75.65	78.01
YIELDS, wt%:				
Coke	3.40	4.33	5.32	6.33
Dry Gas (H_2, C_1-C_2)	4.23	4.99	5.50	5.95
LPG	27.90	30.75	32.19	33.17
Propylene	10.53	11.22	11.46	11.79
Butylenes	9.86	9.88	9.42	8.58
Gasoline (C5-216 °C)	31.89	33.04	32.63	32.57
LCO (216-370 °C)	19.62	17.59	16.37	15.31
Unconverted (above 370	12.97	9.29	7.98	6.67

°C)				
% Liq. Olefins	31.55	22.35	17.56	14.03
% Reduction of liq. Olefins	1.41	17.22	29.76	29.92
% Aromatics	46.03	57.03	63.15	68.13
% Increase in Aromatics	39.951	52.121	59.269	48.788
RON	102.4	105.5	108.6	111.4
Increase in RON Units	7.500	9.400	11.400	13.000

Table 6 shows that the propylene yield has increased and is in the range of (10.53 wt% to 11.79 wt%) and liquid olefin content has decreased (reduction by 1.406% to 29.92%) for all the Catalyst to Vacuum-Gas-Oil ratios as compared to the products of Example 1. At a higher Catalyst to Vacuum-Gas-Oil ratio, the liquid olefin content has decreased significantly. A decrease in the coke yield is also observed when the cat/oil ratio is 3.90. A clear increase in aromatics formation (39.95 % to 59.27 %) and increase in RON units (7.5 units to 13 units) is also observed.

It is found that, using the catalyst composition of the present disclosure, an increase in the propylene yield and in the butylene yield, is obtained in the resultant product, as compared to those of the base catalyst FCC ECAT. This was also accompanied by a reduction in liquid olefin content and the coke yield, especially at higher catalyst to vacuum-gas-oil ratios.

TECHNICAL ADVANCES AND ECONOMICAL SIGNIFICANCE

The present disclosure described herein above has several technical advantages including, but not limited to, the realization of:

- A catalyst composition comprising an additive for a FCC process that provides a product having increased propylene and butylene yields and reduced liquid olefin content; reduced coke yields; with an increase in aromatic yields and the increase in RON units;
- an FCC process that is more profitable; and
- an FCC process that causes reduced fouling of the reactors.

The foregoing description of the specific embodiments will so fully reveal the general nature of the embodiments herein that others can, by applying current knowledge, readily modify

and/or adapt for various applications such specific embodiments without departing from the generic concept, and, therefore, such adaptations and modifications should and are intended to be comprehended within the meaning and range of equivalents of the disclosed embodiments. It is to be understood that the phraseology or terminology employed herein is for the purpose of description and not of limitation. Therefore, while the embodiments herein have been described in terms of preferred embodiments, those skilled in the art will recognize that the embodiments herein can be practiced with modification within the spirit and scope of the embodiments as described herein.

Throughout this specification the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

The use of the expression "at least" or "at least one" suggests the use of one or more elements or ingredients or quantities, as the use may be in the embodiment of the disclosure to achieve one or more of the desired objects or results.

Any discussion of documents, acts, materials, devices, articles or the like that has been included in this specification is solely for the purpose of providing a context for the disclosure. It is not to be taken as an admission that any or all of these matters form a part of the prior art base or were common general knowledge in the field relevant to the disclosure as it existed anywhere before the priority date of this application.

The numerical values mentioned for the various physical parameters, dimensions or quantities are only approximations and it is envisaged that the values ten percent higher/lower than the numerical values assigned to the parameters, dimensions or quantities fall within the scope of the disclosure, unless there is a statement in the specification specific to the contrary.

While considerable emphasis has been placed herein on the components and component parts of the preferred embodiments, it will be appreciated that many embodiments can be made and that many changes can be made in the preferred embodiments without departing from the principles of the disclosure. These and other changes in the preferred embodiment as well as other embodiments of the disclosure will be apparent to those skilled in the art from the

disclosure herein, whereby it is to be distinctly understood that the foregoing descriptive matter is to be interpreted merely as illustrative of the disclosure and not as a limitation.

CLAIMS:

1. An additive for a catalyst composition for a fluid catalytic cracking process comprising a zeolite impregnated with phosphorus in the range of 10 wt% to 15wt% with respect to the weight of said zeolite and a mixture of metal promoters comprising zirconium, molybdenum, nickel, cobalt, zinc and gallium, independently in the range of 0.1 wt% to 1.0 wt% with respect to the weight of said zeolite.

2. The additive as claimed in claim 1, wherein said phosphorous in said zeolite is 12 wt% with respect to the weight of said zeolite.

3. The additive as claimed in claim 1, wherein the precursor of phosphorus is at least one phosphorus compound selected from the group consisting of phosphoric acid, phosphates, phosphorous acid, phosphites, pyrophosphoric acid, pyrophosphates, polymeric phosphoric acid, polyphosphates, metaphosphoric acid and metaphosphates.

4. The additive as claimed in claim 1, wherein the amount of said metal promoters with respect to the weight of said zeolite are:
    a. 0.5 wt% zirconium;
    b. 0.5 wt% molybdenum;
    c. 0.5 wt% nickel;
    d. 0.5 wt% cobalt;
    e. 1 wt% zinc; and
    f. 1 wt% gallium.

5. The additive as claimed in claim 1, wherein the precursor for each of the said metal promoter is a nitrate salt of said the respective metal.

6. The additive as claimed in claim 1, wherein said zeolite is at least one selected from the group consisting of ZSM-5, ZSM-11, ZSM-12, ZSM-48, ZSM-57, SAPO-5, SAPO-11, SAPO-17, SAPO-18, SAPO-34, SAPO-44, MCM-22, ZSM-Y and zeolite-Beta.

7. A catalyst composition for a fluid catalytic cracking process comprising an FCC equilibrated catalyst (ECAT) in the range of 80 wt% to 99 wt% and an additive as claimed in claim 1, in the range of 1 wt% to 20 wt%.

8. The catalyst as claimed in claim 7, wherein the amount of said FCC equilibrated catalyst (ECAT) and said additive is at least one selected from:

   a. 85 wt % of said FCC equilibrated catalyst (ECAT) and 15 wt% of said additive; and

   b. 93 wt % of said FCC equilibrated catalyst (ECAT) and 7 wt% of said additive.

9. A fluid catalytic cracking process for obtaining cracked run naphtha from vacuum gas oil, using the catalyst composition as claimed in claim 7, said process comprising treating the vacuum gas oil in a reactor maintained at a temperature in the range of 400 °C to 750 °C and at a pressure ranging from 1 atm to 2 atm, to obtain a resultant product,
   wherein the catalyst to vacuum-gas-oil ratio is in the range of 1 to 10 wt/wt.

10. The process as claimed in claim 9, wherein the resultant product containes at least one of propylene yield in the range of 7 % to 16 %, butylene in the range of 8 % to 10 %, a liquid olefin content in the range of 10 % to 45 %, RON in the range of 95 to 115 and aromatics content in the range of 40 % to 70 % and a coke content in the range of 2 % to 7 %.

11. The process as claimed in claim 9, wherein said reactor is a fixed fluid bed reactor.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2016/053220

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J27/16 B01J29/06 B01J29/40 B01J29/48 B01J37/00
B01J37/02 C10G11/05
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2015/165427 A1 (AWAYSSA OMAR RATIB [SA] ET AL) 18 June 2015 (2015-06-18) paragraphs [0002], [0010], [0013], [0015], [0016], [0037], [0040] table 2	1-11
Y	US 5 041 402 A (CASCI JOHN LEONELLO [GB] ET AL) 20 August 1991 (1991-08-20) column 20, line 21 - line 22	1-11
Y	US 2011/120912 A1 (BOURANE ABDENNOUR [SA] ET AL) 26 May 2011 (2011-05-26) claims 5-7	1-11
Y	WO 2015/001004 A1 (TOTAL RES & TECHNOLOGY FELUY [BE]; CENTRE NAT RECH SCIENT [FR]) 8 January 2015 (2015-01-08) page 10, line 9 - line 16	1-11

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 August 2016	19/08/2016

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Zieba, Roman

1

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2016/053220

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2010/230324 A1 (AL-ALLOUSH SAEED SAAD [SA] ET AL) 16 September 2010 (2010-09-16) paragraph [0051]	1-11
Y	US 2009/124842 A1 (REAGAN WILLIAM J [US] ET AL) 14 May 2009 (2009-05-14) claim 2	1-11

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2016/053220

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2015165427 A1	18-06-2015	NONE	
US 5041402 A	20-08-1991	AU 622964 B2	30-04-1992
		AU 4714689 A	28-06-1990
		CA 2006542 A1	22-06-1990
		CN 1044052 A	25-07-1990
		DE 68903560 D1	24-12-1992
		DE 68903560 T2	17-06-1993
		DK 654789 A	23-06-1990
		EP 0378916 A1	25-07-1990
		ES 2044151 T3	01-01-1994
		GR 3006777 T3	30-06-1993
		IN 178832 B	05-07-1997
		JP 2924911 B2	26-07-1999
		JP H02222727 A	05-09-1990
		NO 895175 A	25-06-1990
		RU 2067024 C1	27-09-1996
		US 5041402 A	20-08-1991
		US 5345021 A	06-09-1994
		ZA 8909697 B	27-03-1991
US 2011120912 A1	26-05-2011	CN 102281944 A	14-12-2011
		CN 105148895 A	16-12-2015
		EP 2310122 A1	20-04-2011
		JP 5744731 B2	08-07-2015
		JP 2012503032 A	02-02-2012
		US 2011120912 A1	26-05-2011
		WO 2010014256 A1	04-02-2010
WO 2015001004 A1	08-01-2015	CN 105517708 A	20-04-2016
		EP 3016738 A1	11-05-2016
		KR 20160027199 A	09-03-2016
		US 2016136625 A1	19-05-2016
		WO 2015001004 A1	08-01-2015
US 2010230324 A1	16-09-2010	CN 102947423 A	27-02-2013
		EP 2576733 A1	10-04-2013
		US 2010230324 A1	16-09-2010
		WO 2011149763 A1	01-12-2011
US 2009124842 A1	14-05-2009	NONE	