WPC Tomorrow’s Leaders Symposium 2015

«New Russian technologies in the field of refining and petrochemistry»

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The main directions of development of oil refining and petrochemistry in Russia

1. Increasing the depth of refining
2. Improving the environmental performance of the fuels (Euro-5)
3. Processing of associated petroleum gas and methane
4. Processing of heavy raw material
5. Development of new processes and catalysts
Increasing the depth of processing
### Hydroconversion of heavy residues at the nanoscale catalysts

**Developers:** TIPS RAS, IPCP RAS and IMET URO RAN

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Hydroconversion INHS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conditions of process:</td>
<td></td>
</tr>
<tr>
<td>- pressure, MPa</td>
<td>7.0-8.0</td>
</tr>
<tr>
<td>- temperature, °C</td>
<td>440-450</td>
</tr>
<tr>
<td>Conversion, % mass</td>
<td>95.0</td>
</tr>
<tr>
<td>Amount of catalyst, % mass</td>
<td>0.05</td>
</tr>
</tbody>
</table>

**Information of TIPS RAS**

**Implementation:**
- JSC «Transneft» - 50 th. T/y (it was developed a basic project)

**Will be implemented:**
- JSC «Gazprom» (Astrakhan) – 800 th. T/y
- JSC «Gazpromneft» (Moscow) – 2.0 million T/y
- JSC «Ilskiy Refinery»
Catalytic cracking of vacuum gasoil (JSC «TAIF-NK»)

Developers: TIPS RAS, JSC «VNIPIneft», JSC «VNIINP»

The main advantages of the technology:

- Flexible processing of vacuum gasoil
- During the processing according to petrol variant:
  - The yield of gasoline end boiling point of 205 °C - 56% by weight.
  - The total yield of propane-propylene and butane-butylene fraction, gasoline and light gasoil - 87.5% by weight.
  - Octane number determined by analytical method - 94.2
  - Consumption of fresh catalyst, - at least 0.5 kg / ton. of raw materials
Advantages of the technology:

- The technology does not use water and water vapor, which prevents the formation of effluents
- Continuous running of the installation is not less than 1 year
- Option with the reaction chamber requires lower capital and operating expenses
- Best distillate compared to thermal cracking and delayed coking (minimal content of aromatic and unsaturated hydrocarbons)
Hydrocracking with increased yields of diesel fuel by aluminosilicate catalysts

Process conditions: 410 °C; 10,0 MPa; 0,73 hour⁻¹; H₂/ feedstock 1130 nm³/m³

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion GED, %</th>
<th>Output of diesel fuel, %</th>
<th>S at residue, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>ИК</td>
<td>82,0</td>
<td>67,5</td>
<td>50</td>
</tr>
<tr>
<td>Imported</td>
<td>75,5</td>
<td>61,5</td>
<td>60</td>
</tr>
<tr>
<td>Russian</td>
<td>67,0</td>
<td>53,0</td>
<td>70</td>
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</tbody>
</table>
Improving the environmental performance of the fuels (Euro-5)
Combination of heterogeneous-catalyzed reaction with simultaneously conducted distilling or fractionating on catalyst layer.

Catalyst in size from 0.25 to 1 mm contains in porous tanks like canvas tank, wire-mesh sections or polymer fabrics. Hydrocracking with increased outcrop of diesel gasoil on silica-alumina catalyst.

The main developers: BASF, Katalitik distilleyshn Technologies, Research & Chemical Company laysensing, CD-tech, PRIS.
Isomerization technology of light gasoline fractions

Developer: JSC «SIE Neftehim»

Key benefits:
- High-activity catalyst in resistance to S, N, H₂O
- Does not require a supply for an acid component
- Low chemical consumption of hydrogen
- Full recoverability of the catalyst after regeneration
- Catalyst life – 10 years
- Cycle length – 3 years

Catalysts: CI-2; Pt + ZrO₂ + SO₄²⁻

Implementation:
- JSC "Slavneft-Yaroslavnefteorgsintez"
- JSC "Gazpromneft-Omsk Refinery"
- JSC "LUKOIL Ukhtaneftepererabotka"
- JSC "Petrotel-LUKOIL"
- JSC "Novoil"
- JSC "Linnik"
- JSC "Ufaneftekhim"
Hydrodeparaffinization results of different types of raw materials on the catalyst SGK-1

I - kerosine fraction, II - diesel fraction, III - gasoil of catalytic cracking

<table>
<thead>
<tr>
<th>Показатели</th>
<th>I (сырьё)</th>
<th>гидрогенизат</th>
<th>II (сырьё)</th>
<th>гидрогенизат</th>
<th>III (сырьё)</th>
<th>гидрогенизат</th>
</tr>
</thead>
<tbody>
<tr>
<td>Температура процесса, °C</td>
<td>315</td>
<td></td>
<td>320</td>
<td></td>
<td>340</td>
<td></td>
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<tr>
<td>Фракционный состав, °C:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- н.к.</td>
<td>168</td>
<td>167</td>
<td>195</td>
<td>163</td>
<td>160</td>
<td>160</td>
</tr>
<tr>
<td>- 10%</td>
<td>180</td>
<td>205</td>
<td>230</td>
<td>209</td>
<td>146</td>
<td>191</td>
</tr>
<tr>
<td>- 50%</td>
<td>215</td>
<td>218</td>
<td>278</td>
<td>275</td>
<td>240</td>
<td>229</td>
</tr>
<tr>
<td>- 90%</td>
<td>261</td>
<td>261</td>
<td>335</td>
<td>337</td>
<td>293</td>
<td>230</td>
</tr>
<tr>
<td>- 98%</td>
<td>282</td>
<td>285</td>
<td>359</td>
<td>346</td>
<td>323</td>
<td>316</td>
</tr>
<tr>
<td>Содержание н-алканов, %</td>
<td>21,0</td>
<td></td>
<td>17,0</td>
<td>2,5</td>
<td>8,1</td>
<td>1,2</td>
</tr>
<tr>
<td>Температура, °C:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- застывания</td>
<td>-</td>
<td></td>
<td>-12</td>
<td>-50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>- кристаллизации</td>
<td>-36</td>
<td>-60</td>
<td>-</td>
<td>-</td>
<td>-3</td>
<td>-60</td>
</tr>
<tr>
<td>Выход, %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- C₁–C₄</td>
<td>-</td>
<td>5,8</td>
<td>-</td>
<td>5,5</td>
<td>-</td>
<td>4,0</td>
</tr>
<tr>
<td>- C₅–160°C</td>
<td>-</td>
<td>18,2</td>
<td>-</td>
<td>10,6</td>
<td>-</td>
<td>8,5</td>
</tr>
<tr>
<td>- фракции 160°C – к.к.</td>
<td>-</td>
<td>74,2</td>
<td>-</td>
<td>82,5</td>
<td>-</td>
<td>86,5</td>
</tr>
<tr>
<td>Потери, %</td>
<td>-</td>
<td>1,5</td>
<td>-</td>
<td>1,4</td>
<td>-</td>
<td>1,0</td>
</tr>
</tbody>
</table>

P – 4,0 MPa, Vc – 1,0 hours⁻¹
The main advantages of the technology:

- Improving the quality of marketable products:
  - Obtaining hydrocarbonated gasoline fraction of catalytic cracking with sulfur content not exceeding 100 ppm
  - Reduction of up to 30 ppm of hydrogen sulfide (H2S) and sour sulfur to 0.002% by weight to obtain fractions of PPF and BBF
- Reduction of harmful impacts on the environment
- Creation of possibilities for increasing the capacity of the enterprise.
Processing of associated petroleum gas and methane
Oxidative condensation of methane (IGIC, Gubkin University, TIPS)

2 CH₄ → O₂, N₂O, [O]₅

C₂H₄ + 2 H₂O

C₂H₄, C₂H₆ – base products
H₂; CO; CO₂; H₂O – co-products

Parameters of converting methane

<table>
<thead>
<tr>
<th></th>
<th>In the world</th>
<th>In Russia</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane conversion, %</td>
<td>20-37</td>
<td>50</td>
</tr>
<tr>
<td>Products output C₂+, %</td>
<td>16 (26*)</td>
<td>30</td>
</tr>
</tbody>
</table>

Oxidative condensation of methane:

Initial mixture (NG*+O₂) → Steam → Crude ethylene → CO₂

Recycle of the processing unit

To refining
Processes of producing olefins from natural gas (TIPS RAS, IPCP RAS)

- **Natural Gas** → **Synthetic gas**
  - Production of methanol
    - UOP (USA), TIPS RAS, IPCP RAS
  - Production of DME
    - TIPS RAS, IPCP RAS
  - Synthesis of olefins in a fluidized bed
    - SAPO-34/18
  - Synthesis of olefins in a stationary bed
    - ZSM-5

- **Production of methanol**
  - Ethylene (34-49%) → Propylene (26-44%)

- **Production of DME**
  - Ethylene (< 40%) → Propylene (< 45%)
<table>
<thead>
<tr>
<th>Process</th>
<th>Conversion</th>
<th>Step of olefin synthesis</th>
<th>C2-C4 olefins, %</th>
<th>Selectivity</th>
<th>Possible other products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Catalyst</td>
<td>T,°C</td>
<td>%</td>
<td>C2=</td>
</tr>
<tr>
<td>Pyrolysis</td>
<td>70</td>
<td>-</td>
<td>1000</td>
<td>&gt;99</td>
<td>47</td>
</tr>
<tr>
<td>Mobil</td>
<td>50-70</td>
<td>ZSM-5</td>
<td>350-400</td>
<td>47-75</td>
<td>26-56</td>
</tr>
<tr>
<td>UOP/Norsk-hydro</td>
<td>70</td>
<td>SAPO-34</td>
<td>450</td>
<td>&lt;100</td>
<td>75-90</td>
</tr>
<tr>
<td>Lurgi (DME)</td>
<td>70</td>
<td>ZSM-5</td>
<td>430-450</td>
<td>99</td>
<td>&gt;69</td>
</tr>
<tr>
<td>Van Dijk (DME)</td>
<td>-</td>
<td>SAPO-34</td>
<td>450</td>
<td>70</td>
<td>49</td>
</tr>
<tr>
<td>DME из SG INHS; IPHF</td>
<td>&gt;80</td>
<td>ZSM-5</td>
<td>340-450</td>
<td>95-100</td>
<td>80-88</td>
</tr>
</tbody>
</table>
TIPS RAS process for producing liquid hydrocarbon mixtures according to Fischer-Tropsch

C10-C20, catalyst

100 Fe:3K2O:8Al2O3

Synthetic gas

CO conversion 90%
C5+ selectivity 70%
CH4 selectivity < 5%
Development of new processes and catalysts
Alkylation on solid catalysts

- The TIPS Russian Academy of Sciences developed the alkylation process on a solid catalyst, which has been tested on the pilot industrial plant:
  - fixed bed of zeolite catalyst TTSM-38
  - Average temperature of 40 - 100 °C
  - Pressure of 1.0 - 1.7 MPa
  - Catalyst consumption of 0.2 - 0.3 kg / t alkylbenzene
  - Octane alkylate target 96 - 98 (AMI)
  - Time of the catalyst without regeneration up to 48 hours
  - Regeneration is carried out in a hydrogen stream
BIC SB RAS technology of hydrotreatment catalyst activity restoration

Degree of hydodesulfurization, %

- Fresh catalyst
- Deactivated catalyst
- Oxidative regeneration
- After regeneration
- Activation
- After activation

- 99.9%
- 97.0%
- 98.5%
- 99.9%
- 10 ppm S
- 300 ppm S
- 10 ppm S
New industrial reforming catalyst

Institute of Hydrocarbon Processing SB RAS (Omsk) and JSC "NPP Neftehim" (Krasnodar), created a new reforming catalyst PR-81.

PR-81 - trimetallic catalyst which provides enhanced stability while maintaining activity and selectivity of their predecessors.

Key indicators in reforming francs. 85-1800S to produce gasoline with RON 95

<table>
<thead>
<tr>
<th></th>
<th>Average level in Europe</th>
<th>PR-51, 71</th>
<th>PR-81</th>
</tr>
</thead>
<tbody>
<tr>
<td>The yield of reformate, % mass.</td>
<td>82-85</td>
<td>86-88</td>
<td>90</td>
</tr>
<tr>
<td>The yield of hydrogen, % mass.</td>
<td>1,6-2,0</td>
<td>2,4-2,6</td>
<td>2,8</td>
</tr>
<tr>
<td>The hydrogen concentration in WASH% vol.</td>
<td>73-80</td>
<td>83-86</td>
<td>86</td>
</tr>
<tr>
<td>Average integral temperature °C</td>
<td>480</td>
<td>470</td>
<td>465</td>
</tr>
<tr>
<td>The octane number, RON</td>
<td>95-98</td>
<td>95-98</td>
<td>98-100</td>
</tr>
</tbody>
</table>

Data: IPPU SB RAS
Thank you for your attention!

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