Institute of Petroleum Refining and Petrochemistry

# NEW TECHNOLOGIES IN PETROCHEMICAL PRODUCTION

2020

# Technologies under supercritical conditions

Drawbacks of the traditional technology:

- Large number of process operations (minimum 3 stages)
- Relatively low target product yield
- Need for separation and disposal of by-products (acid waste etc.)
- Process time (over 24 hours)

Advantages of a new technology:

- One stage
- No catalysts
- Environmental friendliness
- Simple hardware
- Significant production cost reduction

# Production of carboxylic acid compound ethers

### Dioctyl terephthalate (DOTP)

| Component name | % wt. |
|---|---|
| Octylisophthalate | 0,34 |
| Dioctylterephthalate (DOTP) | 91,10 |
| Water | 8,56 |
| Total | 100 |

### Dioctyl sebate (DOS)

| Component name | % wt. |
|---|---|
| Dioctyl sebacate (DOS) | 85,28 |
| Octylsebacate | 7,11 |
| Water | 7,61 |
| Total | 100 |

### Dioctyl adipate ester (DOA)

| Component name | % wt. |
|---|---|
| Dioctyl adipate (DOA) | 86,11 |
| Octyladipate | 7,61 |
| Water | 6,28 |
| Total | 100 |

### Acetic ether (ethyl acetate)

| Component name | % wt. |
|---|---|
| Ethanol | 3,31 |
| Acetic acid | 9,89 |
| Ethyl acetate | 74,20 |
| Water | 12,58 |
| Total | 100 |

### Propyl acetic ester (propyl acetate)

| Component name | % wt. |
|---|---|
| Propanol-1 | 2,49 |
| Acetic acid | 2,51 |
| Propyl acetate | 80,75 |
| Water | 14,25 |
| Total | 100 |

### Butyl acetic ester (butyl acetate)

| Component name | % wt. |
|---|---|
| Butanol-1 | 3,31 |
| Acetic acid | 2,68 |
| Butyl acetate | 81,37 |
| Water | 12,62 |
| Total | 100 |

# Isoprene production technology under supercritical conditions

The isoprene production technology is based on Diels-Alder reaction reaction under supercritical conditions:

Piperylene/ethylene = 1/10; $T_{cr}$, $P_{cr}$;

isoprene yield  per passed piperylene 51 % wt.

# Fatty acid ethyl ester (biodiesel) production technologies

The biodiesel production technology is based on reesterification of fat acids triglycerides (FAT - sunflower oil) by ethyl alcohol under supercritical conditions (catalyst-free process)

| Component name, % wt. | Contents, % wt. |
|---|---|
| Mole ratio, FAT : alcohol | 1:6 |
| Fat acid ethyl ester (FAEE) | 43.78 |
| Glycerine | 13.71 |
| Fat acid triglyceride (FAT) | 7.82 |
| Ethanol | 34.29 |
| Total | 100 |

<u>Advantages</u>

- Biofuel has excellent lubricating properties
- Fuel spills are quickly decomposed by micro-organisms
- Biodiesel production simplicity, low price and speed
- No strong smell and a low toxicity level

# Heterogeneous catalyst regeneration technology

The main drawbacks of the traditional oxidation regeneration –
high temperature and oxidizing medium – have a negative impact on a catalyst structure reducing a catalyst operating life

The process of regeneration by supercritical fluids enables to extract coke deposits from catalyst pores without changing its morphological and textural characteristics

Advantages of the technology

- no effluents, emissions, solid waste
- low power consumption
- simple process equipment
- possibility for regeneration of all heterogeneous oil refining and petrochemistry catalysts
- catalyst life cycle increase

Example

| Medium temperature isomerization catalyst | | |
|---|---|---|
| | Traditional regeneration | New technology |
| Physical and chemical catalyst properties (morphology and texture) | irreversible changes, catalyst structure integrity violation, "ageing" | does not change |
| Conversion, % wt. | 68.7 | 69.89 |
| Selectivity, % wt. | 93.9 | 94.14 |
| Yield % wt. | 64.7 | 65.46 |
| Catalyst operating life | 8 years | 12-15 years |

# Isobutane olefin solid acid alkylation technology

## Isobutane olefin alkylation on zeolitic catalysts with in situ regeneration

| | Technology with sulphuric acid | New technology |
|---|---|---|
| Capital investments | 100 % | 50% |
| Yield (g/y of olefins) | | |
| Alkylate yield | 1.78 | 1.92 |
| Isobutane consumption | 1.17 | 1.23 |
| RON (research octane number) | 95 | 96-97 |
| Auxiliary resources/ materials (per alkylate barrel) | | |
| Vapour (kg) | 90.72 | 107.5 |
| Electric power (kW-) | 10.5 | 3.5 |
| Cooling water (thous. $m^3$) | 8.33 | 0.87 |
| Catalyst (kg) | 9.07 | 0.05 |
| NaOH (100%, kg) | 0.05 | - |

- The continuous mode of the alkylation process on a heterogeneous catalyst has been developed
- It combines sequential alternation of traditional and supercritical conditions with the option of "in situ" regeneration
- It enables to increase significantly cycle length and efficiency of zeolitic catalyst during the isobutane fraction alkylation process
- Experimental-pilot runs verifying catalyst stable operation, over 1000 hours, were performed

# Development of new petrochemistry and oil refining technologies

## Gasoline fraction aromatization technology

| Hydrocarbons | Feedstock, % wt. | Products, % wt. |
|---|---|---|
| $C_1$-$C_4$ | - | 29.67 |
| Gasoline fraction (nk-180 °C) | 91.0 | 63.31 |
| Kerosene fr. (180-kk °C) | 9.0 | 7.02 |
| Total | 100.0 | 100.0 |


## Pentane fraction medium temperature isomerization technology

| Hydrocarbons | Feedstock, % wt. | Products, % wt. |
|---|---|---|
| $C_3$-$C_4$ | - | 1.13 |
| Hydrogen | 6.90 | 6.42 |
| Pentane | 100 | 33.31 |
| Isopentane | - | 66.04 |
| Total | 106.90 | 106.90 |

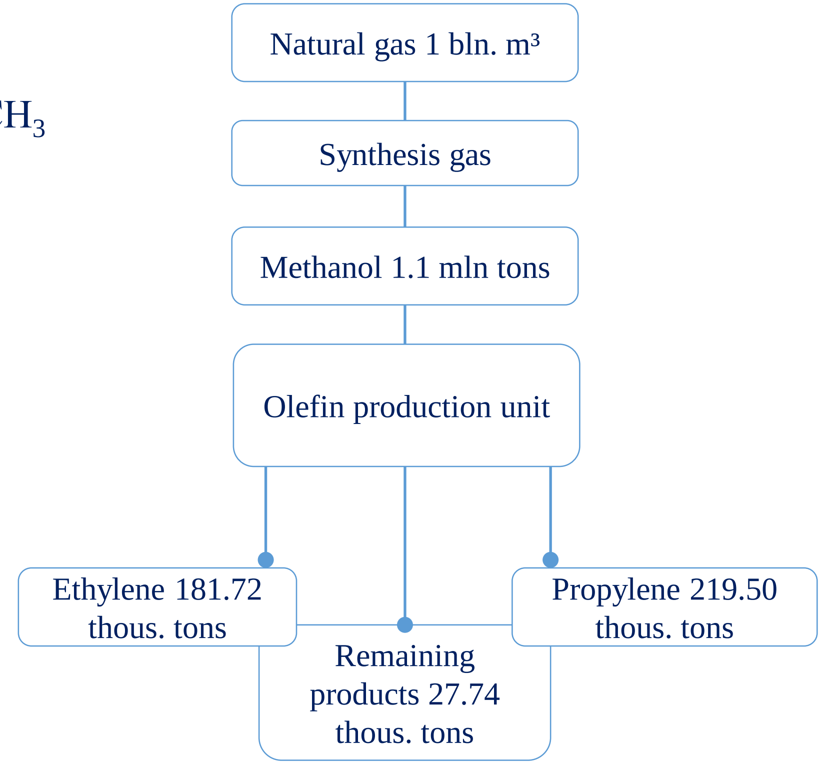
The gas condensate residual fraction hydrocatalytic process refining technology

| Hydrocarbons | Feedstock, % wt. | Per pass,% wt. | With residue recirculation, % wt. |
|---|---|---|---|
| $C_1$-$C_4$ | - | 6.24 | 7.48 |
| Gasoline fraction (nk-160°C) | 4.50 | 11.50 | 12.63 |
| Kerosene fr. (160-240°C) | 7.90 | 17.00 | 20.34 |
| Diesel fr. (240-350°C) | 30.30 | 46.86 | 52.43 |
| Residue 350 °C+ | 57.30 | 18.40 | 7.12 |
| Total | 100.00 | 100.00 | 100.00 |

# Domestic catalyst based on SAPO-34 for a logistics process

$$\underset{\text{methanol}}{CH_3OH} \xrightarrow{\text{catalyst}} \underset{\text{ethylene}}{CH_2{=}CH_2} + \underset{\text{propylene}}{CH_2{=}CH-CH_3}$$

| T, °C | Ethylene yield, % wt. |
|---|---|
| 380 | 16.52 |
| 400 | 14.41 |
| 420 | 13.92 |



# Propane-propylene (PPF) and butane-butylene fraction (BBF) oligomerization technology and catalysts

Composition of oligomerizate, parameters and indicators of PPF and BBF oligomerization process on a superacid catalyst based on pillared montmorillonite

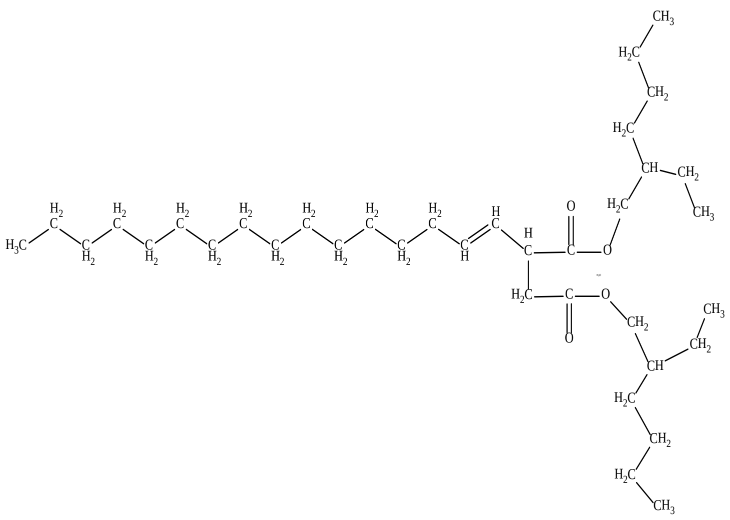
| Composition of oligomerizate: | PPF | BBF |
|---|---|---|
| $C_6$ | 15.1 | 2.4 |
| $C_7$ | 2.8 | 3.1 |
| $C_8$ | 3.3 | 40.8 |
| $C_9$ | 47.2 | 7.5 |
| $C_{10}$ | 2.1 | 11.4 |
| $C_{11}$ | 1.7 | 2.3 |
| $C_{12+}$ | 27.8 | 32.5 |
| Total | 100 | 100 |
| Parameters and indicators of process: | | |
| Temperature, °C | 150 | 150 |
| Pressure, MPa | 3.0 | 4.0 |
| Feedstock delivery speed, $h^{-1}$ | 1 | 1 |
| Olefin conversion degree α, % | 68.1 | 70.8 |

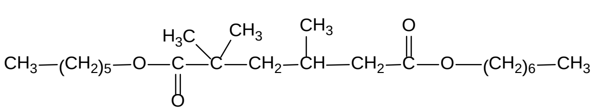
# Additives to motor oils and fuels

| №№ | Additive name | Additive characteristics |
|---|---|---|
| 1 | **ALKENYLSUCCINAMIDE** | Base number - 30<br>Nitrogen contents – 2.1<br>Kinematic viscosity at 100 °C – 90 $mm^2/c$<br>Active substance – 40.0<br>$T_{flash}$ = 196 °C<br>Detergent properties, score – 0.5<br>Corrosive properties, score – 5.0<br>Lubricating capacity: adjusted wear scar diameter at 60 °C, 398 mcm (0.1% wt.) |
| 2 | **ALKYL PHENOL** | Reduction of I-40 oil pour point during the addition of 1% additive<br>Kinematic viscosity at 100 °C – 8.5 $mm^2/c$<br>Acid number – 0.3<br>I-40 oil corrosiveness with 1% additive on lead plates – 10 $g/m^3$ |

# Synthetic oils based on dicarboxylic acid esters, compound complex esters and alkyl naphthalenes

| №№ | Synthetic oil type | Synthetic oil characteristics |
|---|---|---|
| 1 | Alkyl naphtalene | $T_{pour.}$ = - 45 °C<br>Density at 20°C = 0.978 g/cm³<br>Kinematic viscosity at 100°C – 4.38 mm²/c<br>Kinematic viscosity at 40°C – 26.10 mm²/c<br>Viscosity index – 58 |
| 2 | Dicarboxylic acid esters | $T_{pour.}$ = - 64 °C<br>Density at 20°C = 0.964 g/cm³<br>Kinematic viscosity at 100°C – 3.2 mm²/s<br>Kinematic viscosity at 40°C – 18.5 mm²/c<br>Viscosity index – 67 |
| 3 | Complex alkenylsuccinic anhydride esters | $T_{pour.}$ = - 46 °C<br>Density at 20°C = 0.978 g/cm³<br>Kinematic viscosity at 100°C – 12.39 mm²/s<br>Kinematic viscosity at 40°C – 56.23 mm²/s<br>Viscosity index – 26 |





**Results of the comparative analysis of mixture properties using essential and polyalphaolefin oils (Nexbase-2004)**

| № | | Sample №1 | Sample №2 | Sample №3 | Sample №4 | Sample №5 |
|---|---|---|---|---|---|---|
| 1 | I-20A with thickener Infineum SV-260 | up to 100% | up to 100% | up to 100% | up to 100% | up to 100% |
| 2 | Nexbase-2004, % wt. | - | 10 | - | - | - |
| 3 | EO, % wt. | - | - | 8 | 10 | 15 |
| 4 | Kinematic viscosity at 100 °C | 14.67 | 14.28 | 14.27 | 14.32 | 14.12 |
| 5 | Kinematic viscosity at 40 °C | 105.56 | 97.61 | 100.34 | 102.27 | 96.42 |
| 6 | Viscosity index | 128 | 131 | 133 | 130 | 132 |
| 7 | CCS at -25°C (maximum 7000) | 10416 | 7352 | 7147 | 6973 | 6905 |