Recent Developments in Petrochemistry, Oil Refinery, Polymers and Membranes
A.V. Topchiev Institute of Petrochemical Synthesis (TIPS RAS) is the part of Russian Academy of Sciences, and was founded in 1934 as Institute of Fossil Fuel. Today, TIPS RAS is a world recognized academic Institute, that has a leading international position in its core areas - Oil Refinery, Petrochemistry, Polymers and Material Science, Membranes and Membrane Technology.

**Strategy**

Combination of multidisciplinary background and high skilled scientists with academic and industrial experience that ensures research towards innovative solutions of every challenging task and needs of modern society and industry.

**Scientific and Education Network**

TIPS RAS has established 8 Research and Education Centers with leading Universities in corresponding areas as well as a number of International Laboratories that allows to sustain leading positions in world academic society by attraction and education of high-skilled and motivated young scientists. TIPS RAS is a member of 4 Russian Technological Platforms.

**Conferences and Seminars**

TIPS RAS traditionally promotes the knowledge exchange and fruitful discussions in scientific community by organizing of the conferences, seminars and being co-founder of three scientific journals (in Russian and English):

- Petroleum Chemistry
- Polymer Science
- Membranes and Membrane Technologies
Catalytic Cracking

Advantages of technology:

• Higher base products yield due to special design of catalytic cracking reactor (control of contact time) in contrast to traditional designs.

• Improved reactor design provides prevention of cracking of base products and reduction of back mixing due to special design of catalyst separation system on an outlet of riser, catalyst and feed contacting system, feed distribution systems.

• Deep catalyst regeneration and lower catalyst consumption due to special design of regenerator unit.

• Failure-free service for 3 and more years without unit stoppage (optimized design of air-spreaders, steam-spreaders, steaming sections, cyclones, firebricks etc.) provides at least extra 3 month of operation.

• Deep expertise and 9 units operating under license allow to provide the best solution for your specific feedstock and needs.

Reference list:

• Burgass Oil Refinery (Bulgaria, 1982), KT-1 unit
• Moscow Oil Refinery (Russia, 1983), G-43-107 unit
• Pavlodar Oil Refinery (Kazakhstan, 1983), KT-1 unit
• Mazheky Oil Refinery (Lithuania, 1989), KT-1 unit
• Omsk Oil Refinery (Russia, 1994), KT-1 unit
• New Baku Oil Refinery (Azerbaijan, 1994), G-43-107 unit
• "Upha-petrochem“ (Russia, 1995), G-43-107 unit
• Lisichansk Oil Refinery (Ukraine, 1995), G-43-107 unit
• "TAIF-NC“ (Russia, 2006), G-43-107 unit
Alkylate Production on Solid Catalysts

Alkylation of iso-butane by olefins:
- High octane number: 93-94 (motor method), 96-99 (research method).
- Alkylate has the same octane number characteristics at different boiling temperatures in the range of 40-200°C.
- No aromatic, unsaturated hydrocarbons and S- and O-contained compounds.

Advantages of new process:
- Alkylation of iso-butane with wide range of olefins by using of solid catalysts (high active zeolite catalysts modified by rare earth elements) in contrast to existing industrial processes based on liquid hazardous acids (HF, H₂SO₄).
- “Alkylation in the structured mode”: 3-phases reaction as a result of special regime of vapor-liquid feed mixture operation.
- Service cycle of catalyst – 40 hours (only 2 reactors are required).
- High olefins conversion (98-100%) and product yield (99.8% from theory).
- Catalyst can be produced on industrial scale (pilot-scale catalyst batch was already produced and tested).
- Octane number – up to 98 by research method.
Production of Ethylbenzene and *iso*-Propylbenzene on Solid Catalysts

Ethylbenzene is produced by alkylation of benzene by ethylene. Ethylbenzene is a raw material for styrol production (monomer for polystyrol).

*iso*-Propylbenzene is produced by by alkylation of benzene by propylene. *iso*-Propylbenzene is a raw material for production of phenol and acetone.

Advantages of new alkylation process:

- Environmentally friendly zeolite-based catalysts is used instead of toxic and corrosive one (AlCl₃, H₃PO₄). The catalyst can be produced on industrial level.
- Developed catalysts show high long-term stability (including at least 10 oxidation regenerations).
- Improved alkylation reactor provides uniform temperature profile, high “internal” ratio of benzene:olefin, increasing of catalyst service cycle without losing of activity and selectivity.
- Product yield is >99.5%, olefin conversion – 98-100%.
- Technology is verified on pilot and demo level (Alkar process at Shevchenko plastics plant in Kazakhstan).

Reference list:

- JSC “Gazprom Neftehim Salavat” (Russia, 2003) - ethylbenzene production based on solid catalyst with capacity of 230 000 ton/year.
- JSC “Gazprom Neftehim Salavat” (Russia, 2011) - increasing of ethylbenzene production by 11 500 ton/year due to introduction of transalkylation process based on solid catalyst.
Improved technology of visbreaking process is rather effective for production of good quality residual fuel and byproducts (gas, fraction of gasoline and diesel fuel) due to decomposition of heavy oil residues. Reduced viscosity of oil residues allows to minimize required amount of valuable distillate fractions used for dilution of high-viscous one. Using of improved visbreaking process in oil refining scheme allows to increase recovering of vacuum gasoil from black oil and, hence, to increase the feed stream for catalytic or hydrocracking process.

Additional raw materials for light hydrocarbons production!

Reference list (each unit is ~1.5 million ton/year):
- Omsk (Russia)
- Pavlodar (Kazakhstan)
- Mazhekiy (Lithuania)
- Burgas (Bulgaria)
Hydroconversion of heavy residual is breakthrough in effective processing of tar and heavy oils into synthetic oil. The final product can be used at refineries as additional feedstock for traditional processes of deep oil processing. In addition, the developed technology allows to concentrate and extract the metals (V, Ni, Ca, Mg etc.), contained in initial feed, from the final product.

Heavy residual hydroconversion is based on the new type of catalytic process, so called “colloid” catalysis. Small size catalyst particles are synthesized from the precursor already dispersed in the feed. The size of catalyst particles is much smaller than the average size of the asphaltenes contained in the tar that allows to eliminate the catalyst deactivation due to coke formation on solid catalyst surface.

Any type of crude oil residue can be processed with high conversion (80-95%) regardless the total content of sulfur, metalorganic and asphalt-resinous compounds.
TIPS RAS has developed the technology of effective conversion of syngas produced from natural gas, flare gas or coal to different target product via DME stage:

- **High octane gasoline** (RON=90-92) with low content of aromatic compounds (up to 25-30 wt.%) and durene (less than 1 wt.%).
- **Low aromatic gasoline** with minimum content of aromatic compounds (not higher than 5-8 wt.%) and no paraffins. The product meets all technical requirements to be injected in oil pipe (flare gas utilization in remote areas).
- **Olefines** with high conversion and selectivity for $C_2 - C_4$ (higher than 90%).
Single-stage removal of dissolved oxygen from water

Average concentration of oxygen dissolved in water at room temperature is in the range of 7-10 ppm. Meanwhile, there are strict demands on dissolved oxygen content for several ultrapure water applications:

- Boiler feed water (power plants, <30 ppb $O_2$)
- Semi-conductor industry (<1 ppb $O_2$)
- Food and beverage applications (<20 ppb $O_2$)
- Oil & Gas industry, injection water (50-100 ppb $O_2$)

Break-through technology (with TNO) - catalytic membrane contactor-reactor as a combination of advantages of membrane contactors and packed-bed columns!

Advantages of technology:

- Developed catalytic membrane system allows to effectively remove dissolved oxygen from water in one stage.
- Dissolved oxygen is reacted with hydrogen on the membrane surface coated by Pd. No contamination in water in contrast to traditional approach when sodium sulphite or hydrazine is used.
- Improved coating technique allows to deposit the nano-clusters of Pd onto hydrophobic polymeric porous membranes (without opening of industrial membrane modules) with lower amount of required chemicals.
- No stripping gas – lower energy consumption due to minimum of water evaporation.
- Pilot testing confirmed that dissolved oxygen concentration in water can be reduced lower than 1 ppb.
Antimicrobial hydrocolloid wound dressings

Hydrocolloid wound dressings are used for moderately exuding wounds. Their application enables moist healing of moderately exuding wounds and burns, leg ulcers which helps faster epithelization. One of the main problems in the design of wound dressings is the exudate management: sorption and transport of exudate from the wound surface. Insufficient sorption capacity leads to the drop of dressing adhesion and termination of wearing.

Novel hydrocolloid formulations developed at TIPS RAS contain thoroughly selected components that form an optimized morphology at processing conditions. This combination of composition and morphology of the dressing determines its performance, including mechanical properties (absence of cold flow), excellent exudate management and comfort of wearing for the period of up to 7 days. Translucency of the adhesive allows doctors to observe healing process.

The concept of heat-assisted removal enables easy and atraumatic removal of dressing after short exposure to slightly elevated temperatures (up to 45-46°C).

Antimicrobial activity of the dressings are provided by silver compounds incorporated to their composition. The required silver release profiles can be achieved by fine tuning the composition of the dressing.
Cellulose processing via MMO process and composite cellulose fibers

N-methylmorpholine- N-oxide (MMO) is a direct solvent of cellulose that is used in the process of cellulose fibers manufacturing known as MMO or Lyocell process. This process is an environmentally friendly alternative to the viscose process.

Advantages of technology:

Original solid phase MMO process developed at TIPS RAS presents several important advantages over the traditional Lyocell process: simpler technology with lower number of stages, lower energy consumption, better quality of solution and fibers.

The new method is based upon the solid-phase reaction of cellulose with a crystalline MMO combined with the simultaneous effect of shear deformation and pressure on the system.

The supramolecular structure is of utter importance for the performance of fibers. It can be altered by introduction of various additives. Introduction of specially treated silicate nanoparticles leads to significant increase of tensile strength and modulus without loss of elongation at break due to meso-phase formation. It worth notice that this effect is achieved at concentration of filler as low as 0.03 % wt. Modification of cellulose fibers with nanoparticles does not lead to more complicated technology.

| Content of filler, wt. % |
|---|---|---|---|---|
| Filler particle size, nm | Tensile strength, MPa | Elongation at break, % | Modulus, GPa |
| 0 | N/A | 300-400 | 8-10 | 8-10 |
| 0.03 | 50-100 | 1520 | 9-10 | 30 |
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