

INVESTIGATION OF PRODUCING MODERN BASE OILS

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Modern lube oils are prepared from base oils (base oil mixtures) and additives. The allotted quality parameters and the proper application properties are assured by the harmonical integration of these components. Some key lube oil properties depend on the quality of the base oil. For example a new demand has raised in the area of engine oils in the last couple of years: the demand is to contribute to the lower emission of the vehicles. This means the development of engine oils with low sulphated ash, low metal, sulphur and phosphorous content ("low SAPS" engine oils). In order to reach the adequate properties, the base oil (which is the main component of the engine oils) has to be produced with modern and advanced processes.

The conventional base oil production line has its own disadvantages and limitations, so the catalytic processes were spread to enhance the viscosity index and to reduce the pour point of the base oils. It was necessary to develop and apply base oil production processes and technologies which are flexible to the crude oil quality and can produce environmentally friendly base oils with high viscosity index. To reach these goals the most adequate technologies are the catalytic base oil production processes.

In the experimental section of this paper the results of hydroisomerization of wax from Hungarian crude oil on Pt/zeolite/Al₂O₃ catalyst are presented. Based on our experiments we established that with hydroisomerization base oils with very high or extra high viscosity index and low pour point can be produced from high molecular weight paraffinic hydrocarbon mixture. These base oils with low sulphur and aromatic content are appropriate, for example to produce energy efficient and environmentally friendly engine oils.

Keywords: modern base oils, slack wax, hydroisomerization, Pt/SAPO-11

Introduction

Modern lubricants are prepared basically from base oils (base oil mixtures) and additive(s). The allotted quality parameters and the proper application properties are assured by the harmonical integration of these components. Some key lube oil properties depend on the quality of the base oil.

For example a new demand has raised in the area of engine oils in the recent years: the demand to contribute to the lower emission of the vehicles. This means the development of engine oils with low sulphated ash, low metal, sulphur and phosphorous content ("low SAPS" engine oils). [1-4]. To reach the adequate properties, the base oil (which is the main component of the engine oils) has to be produced with modern and advanced processes.

Table 1 shows the API classification of base oils [5]. The future demand for different quality base oils in the world can be seen in Fig. 1 [6]. Based on this diagram, it can be concluded that the demand for higher quality base oils will slightly increase in the future.

The main requirements of the base oils to make environmentally friendly and high performance level engine oils are [7,8]:

- availability in the proper viscosity grades,
- good viscosity-temperature behaviour
- high viscosity index
- good lubrication properties
- good lubrication quality at low viscosity
- good friction behaviour in wide range of stress,
- good antiwear effect,
- low pour point,
- high flash point,
- good cold flow properties,
- good additive sensitivity,
- low foaming,
- low sulphur content,
- good thermal and oxidation stability in the working range,
- low volatility,
- chemical stability,
- good hydrolytic stability,
- anticorrosion effect,
- non-toxic,

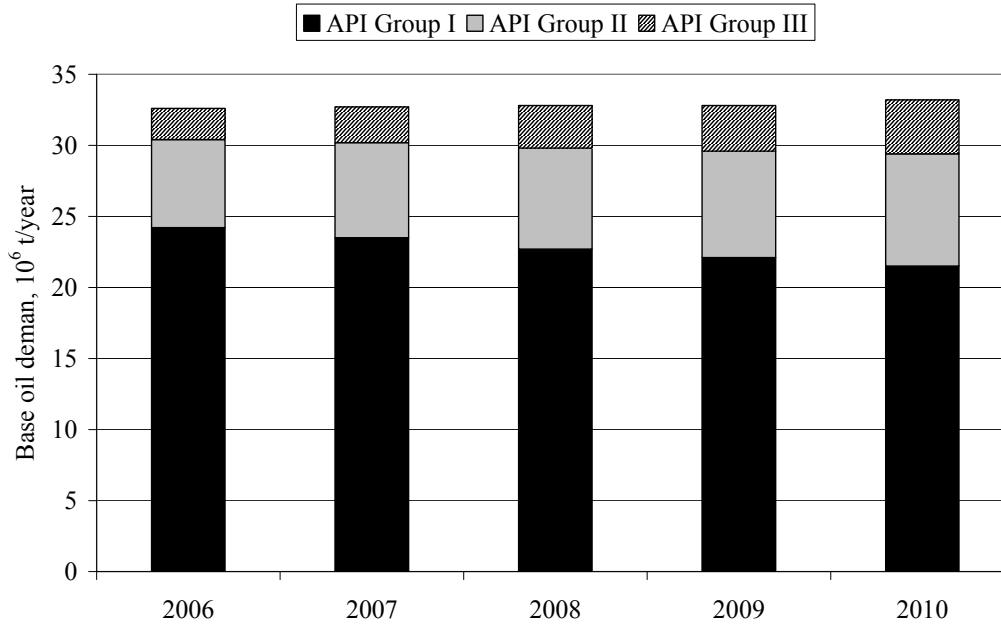


Figure 1: The evolution of world demand for different quality base oils

Table 1: API classification of base oils

Properties	Group				
	I.	II.	III.	IV.	V.
Saturated content, %	<90 and/or	≥90 and	≥90 and	Poli(alfa)-olefins (PAOs)	Every base oil except Group I-IV
Sulphur content, %	>0.03	≤0.03	≤0.03		
Viscosity index (VI)	80≤VI≤120	80≤VI≤120	>120	Chemical synthesis	Chemical synthesis
Typical production technology	Solvent refining	Hydrocracking	Severe hydrocracking, isomerization		

- clean ignition (ashless if possible),
- high additive solvency,
- compatibility with metallic and non-metallic structural materials,
- environmental friendliness and good biodegradability,
- real price etc.

If the engine oil is produced from base oil which fulfils these requirements, the engine will be cleaner and work longer, the oil change period will increase, the fuel consumption will decrease and the activity of the aftertreatment catalytic system will last longer. Today, these properties can be reached with the application of mainly catalytic technologies.

Modern base oils from crude oil

The general process of conventional base oil production contains the following technologies: the vacuum distillation of the atmospheric residue and deasphalting as feedstock production step, solvent refining, solvent dewaxing and a hydrofinishing. However, base oils

produced by this technology line have several disadvantages [5]:

- the yield and the quality of the target product depends on the composition of the crude oil, so the paraffinic crude is strongly preferred;
- the produced base oils have only 100–110 viscosity index, and their pour points are not good enough;
- to produce high performance level (e.g. viscosity index >130–150; volatility <10%) and environmentally benign (low sulphur content, good biodegradability) engine oils very expensive synthetic base oils have to be used,
- from naphthenic crude oil only base oils of low viscosity index can be produced;
- in case of solvent refining the extract can only be used as low value heating oil.

This is the reason why in the last couple of years the catalytic processes kept on spreading in the base oil industry to produce base oils with high viscosity indexes and low pour points. Industry needs base oil production processes which are very flexible to the quality of the feedstocks and can be applied to produce environmentally friendly base oils with high viscosity index.

Base oils with good lubrication properties, containing high amount of multi-branched isoparaffins, having high viscosity index, reduced sulphur and aromatic content (chemically stable), low volatility and good biodegradability can be produced with the following catalytic technologies:

- hydrocracking,
- catalytic dewaxing (n-paraffin conversion),
- isomerization of high molecular weight paraffins,
- hydrotreating and hydroisomerization of the residue of fuel hydrocracking plant,
- severe hydrofinishing.

Nowadays the modern way of base oil production is the application of catalytic processes only (e.g. hydrocracking – catalytic n-paraffin conversion – hydrofinishing) (*Fig. 2*). The product obtained by this way was found to be clean and stable because the molecules with poor lubrication properties are converted to high quality molecules. The value of the pour point and the viscosity index can be controlled properly in the different catalytic steps. Moreover, this kind of technology is flexible, and less sensitive to for the quality of the crude oil [9].

Base oil production from Fischer-Tropsch waxes

The new group of the base oils are the Fischer-Tropsch base oils. The Fischer-Tropsch synthesis is a hydrocarbon producing technology first described in 1923 [10]. The

synthetic crude is at normal conditions is a high pour point (>30–50 °C) hydrocarbon mixture (containing high molecular weight n-paraffins) with zero sulphur and aromatic content. The synthesis and the catalytic conversions can be done with special conditions (reactor structure, catalyst, operating parameters) to produce high amount (10–15%) and high quality feedstocks to produce base oils.

Experimental

In our experiments hydroisomerization of a Hungarian crude slack wax on Pt/SAPO-11/Al₂O₃ catalyst have been carried out. Main goals of these experiments were to produce high quality base oil and high quality gas oil as co-product. Through this process we investigated the effect of the operating conditions on the product yield and quality.

Apparatus

The experiments were carried out in a high-pressure reactor system. This consists of a tubular down-flow reactor of 100 cm³ efficient volume and it is free of back-mixing; it contains equipments and devices applied in the reactor system of industrial plants (pumps, separators, heat exchangers, as well as temperature, pressure and gas flow regulators). The experiments were carried out in continuous operation (*Fig. 3*).

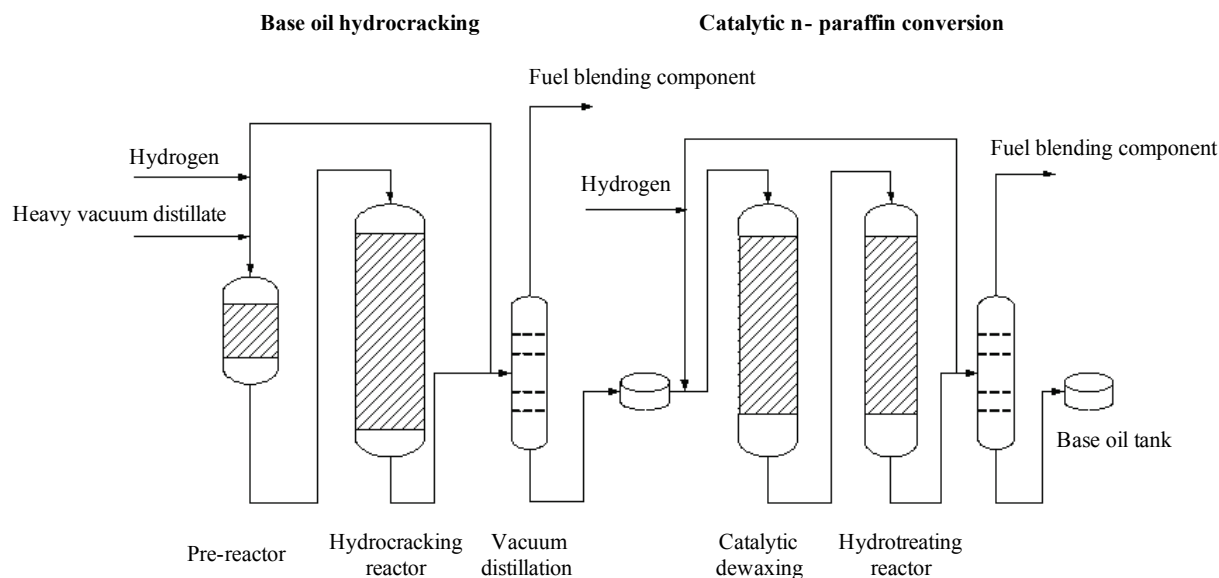


Figure 2: Base oil production by catalytic technologies (simplified scheme)

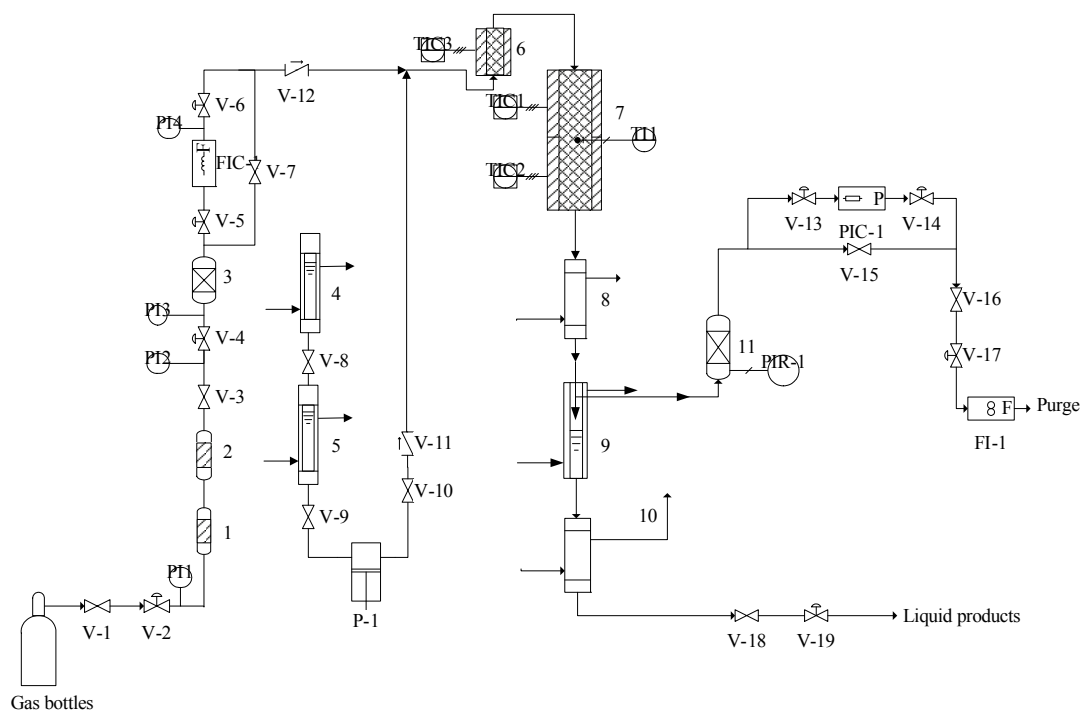


Figure 3: High pressure catalytic experimental apparatus

Catalyst

The experiments were carried out on Pt/SAPO-11/Al₂O₃ catalyst. We chose the ratio of metallic (de- and hydrogenating function) and acidic (skeletal rearranging and selective cracking function) sites of catalyst to produce a low amount of gaseous and naphta products as co-product [11]. Before the experiments the catalyst was activated and dried properly with the method elaborated by us.

Feedstock

The feedstock was crude slack wax obtained from Hungarian crude oil (rich in C₂₂-C₄₀ n-paraffins), which was in solid condition at ambient temperature. The main properties of the feedstock are presented in Table 2.

Table 2: Major properties of the feedstock

Properties	Value
C ₂₀₋ hydrocarbon content, %	9.8
C ₂₀₊ hydrocarbon content, %	90.2
I-/n-paraffin weight ratio	0.41
Pour point, °C	+39
Sulphur content, mg/kg	94
Aromatic content, %	8.5

Process parameters

The applied process parameters were chosen based on the results of previous experiments. They were as follows:

Temperature:	300–380 °C
Pressure:	4.0–8.0 MPa
Liquid hour space velocity:	0.75–3.0 cm ³ /cm ³ _{cat} h
H ₂ /hydrocarbon ratio:	200–600 Nm ³ /m ³

Results and discussion

Based on our experimental results, it is concluded that the Pt/SAPO-11/Al₂O₃ catalyst is applicable to the hydroisomerization of Hungarian slack wax. The degree of hydroisomerization and hydrocracking changed as a function of operational conditions.

The yield of pentanes and heavier products (C₅₊) were 99.5% at the mildest conditions and 73.5% at the strictest conditions. This product was fractionated to naphta, gas oil, base oil and residue fractions. After the gas oil fraction, the base oil fraction was cut in a similar way as their properties fulfil the requirements of API Group III base oils.

The yield of the gaseous and liquid products as a function of process parameters are shown in Fig. 4. These data are typical to the conversion as well.

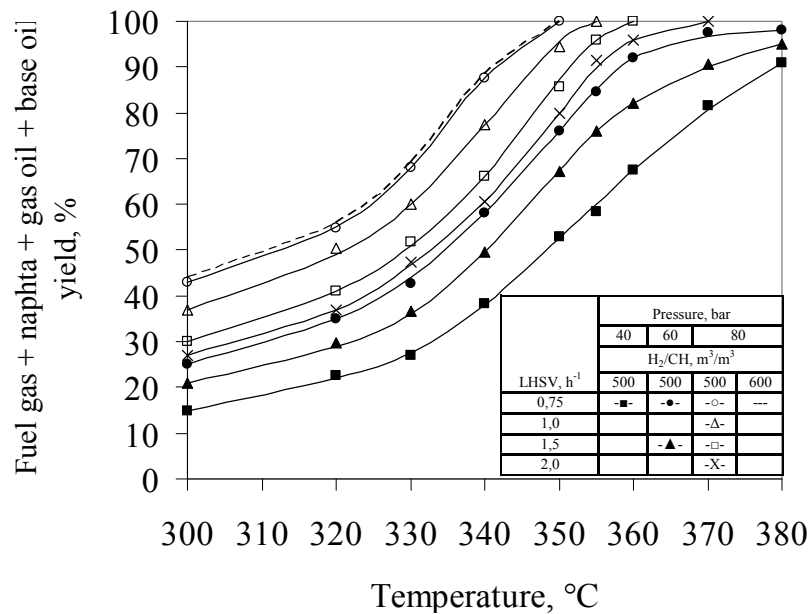


Figure 4: Product yields (fuel gas + naphtha + gas oil + base oil fraction) as a function of temperature

The nearly S-shaped curves show that the depth of conversion increased definitely, but the rate varied in the function of other process parameters. Increase of pressure had positive influence on the catalytic conversion. Decreasing the liquid hour space velocity caused the same tendency. Under the following reaction conditions, namely at 350 °C (and above), 0.75–3.0 h⁻¹ LHSV and 70–80 bar pressure, the products contained no more residue components.

The yield of gaseous products in case of some key process parameter combinations are presented in Fig. 5.

The figure shows that with increasing temperature – at constant other parameters – the gaseous product yield

increased near exponentially. Increasing the liquid hour space velocity, the gaseous product yield decreased at constant other parameters. Using higher pressures, the formation of gaseous products (with significant increasing number of moles) is limited. Increase of the hydrogen/hydrocarbon volume ratio caused the same effect. In the tested process parameter range the amount of gaseous products changed between 0,5% (300 °C, 40 bar, LHSV 3 h⁻¹, 600 m³/m³ hydrogen/hydrocarbon ratio) and 26.5% (380 °C, 40 bar, LHSV 0.75 h⁻¹, 200 m³/m³ hydrogen/hydrocarbon ratio). There has been adverse tendency of changes in the yield of the C₅₊ products, of course.

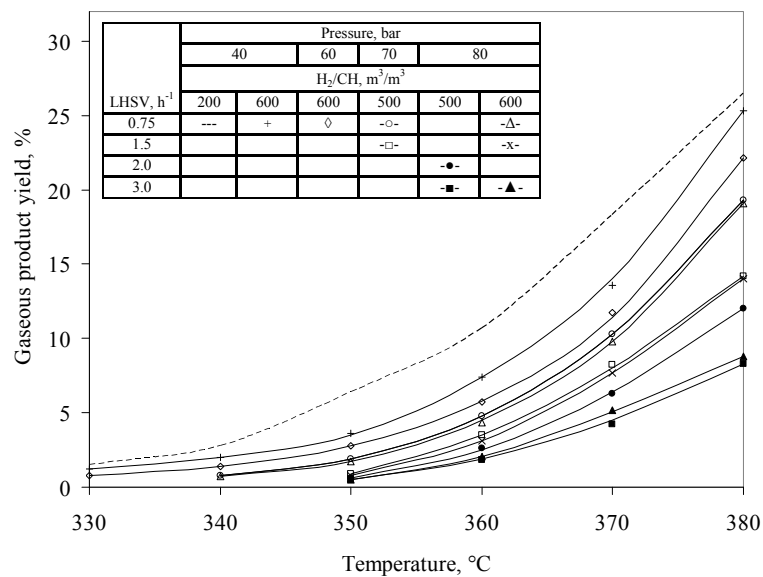


Figure 5: Gaseous product yield as a function of process parameters

As example, the main properties of base oil products, which were produced at advantageous process parameters are presented in *Table 3*. It can be seen, that at optimal process parameters (temperature: 350–355 °C, pressure: 70–80 bar, LHSV: 0.75–1.3, hydrogen/hydrocarbon volume ratio: 500–600 cm³/cm³) base oils having high viscosity index, good cold flow properties, ultra low sulphur content (3–5 ppm) and strongly reduced aromatic content (1.0–3.8%) were produced. These base oils fulfill the requirements of API Group III base oils, and they can be applied to produce lubricants with low sulphur and aromatic content, for example to manufacture “low SAPS” engine oils.

The gas oil products obtained are excellent blending components and fulfil the most severe quality requirements (sulphur content: <2 ppm; cetane number: 61–64, aromatic content: 0.5–1.1%). So they are appropriate to manufacture environmental friendly Diesel fuels. The naphtha fractions, produced in low amount, have high isoparaffine content (>70%) and they are free of sulphur, thus they are considered as excellent naphtha blending components.

Table 3 Main characteristics of isomerized base oils (temperature: 350–355 °C, pressure: 70–80 bar, LHSV: 0.75–1.3, hydrogen/hydrocarbon volume ratio: 500–600 cm³/cm³)

Properties	Value
C ₂₀₋ hydrocarbon content, %	16.9–14.6
C ₂₀₊ hydrocarbon content, %	83.1–86.4
I-/n-paraffin weight ratio	3.29–3.94
Kinematic viscosity (100°C), mm ² /s	3.9–4.15
Viscosity index	136–142
Pour point, °C	-17 (–) -12
Volatility, (Noack), %	14–10
Sulphur content, mg/kg	3–5
Aromatic content, %	1.0–3.8

Conclusions

The principal motivation force behind the base oil development is the growing demand of base oils for the economical production of highly efficient engine oils with practically zero sulphur-, nitrogen- and aromatic content. Base oils possessing these advantageous properties can be produced mostly by catalytic technologies.

Based on the results it can be concluded, that base oils with very high viscosity index and low pour point can be produced from high molecular weight Hungarian crude slack wax with hydroisomerization over the Pt/SAPO-11/Al₂O₃ catalyst. These base oils with low sulphur and aromatic content are appropriate to produce energy efficient and environmentally friendly engine oils.

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