FKIT: OFFICIAL OPENING OF THE LABORATORY FOR PETROLEUM AND PETROCHEMICAL PROCESS ENGINEERING

Abstract

Laboratory for Petroleum and Petrochemical Process Engineering was established as a part of the Petroleum and Petrochemical Department at the Faculty of Chemical engineering and Technology and it was officially opened on July 4, 2011, within the AMACIZ scientific colloquium. The Laboratory was founded with the goal of enabling the research and development of processes treating and refining petroleum fractions and in this way create new opportunities for students for direct and practical training for the work in the petroleum refining industry. Laboratory is used for conducting research and development of separation and catalytic processes and it includes adequate experimental and analytical equipment. Separation processes that are being researched are adsorption and extraction as desulfurization processes for attaining fuels with improved properties in regard to the stringent sulfur content regulations. Laboratory is equipped with four apparatuses for conducting adsorption and extraction experiments in batch and column adsrbers and extractors, respectively. Catalytic conversion experiments are being conducted in an apparatus with fixed bed column reactor and in the presence of hydrogen or some other gas. The experiments can be carried out at temperatures between 25 and 400 °C and pressures between 1 and 40 bars with flow rates for the feed between 0,01 do 10,00 $cm^3\ min^{-1}$ *and for the hydrogen up to 2000* $cm^3\ min^{-1}$*. Laboratory analytical equipment comprises three devices including a gas chromatgraph with flame ionization detector and ZB-1 capillary column for the analysis of hydrocarbons with 1 to 12 C atoms, a wave dispersive x-ray fluorescent spectrometer for elementary analysis of organic liquids and a UV-VIS spectrometer.*

Petroleum and Petrochemical Process Engineering Laboratory was established as a part of the Petroleum and Petrochemical Department at the Faculty of Chemical Engineering and Technology with the aim of conducting research and development of advanced and environmentally friendly petroleum refining and treatment processes which are used to attain petroleum and petrochemical products with improved physical and chemical properties. The formation and equipping of the Laboratory was a gradual process that went on in the period from April, 2008 to November, 2010 when the last piece of equipment was installed. It was officially opened on July 4, 2011, within the AMACIZ scientific colloquium. The Laboratory was established with the help from the Faculty of Chemical Engineering and Technology and from several other financial sources including the Ministry of Science, Education and Sports, through scientific project titled “Advanced processes of hydrocarbon fuels desulfurization” and capital equipment tender, as well as INA – Industrija nafte d.d., through collaboration on projects titled “Desulfurization of FCC gasoline by liquid extraction” and “Optimization of light gasoline isomerization”.

The research in the Laboratory is being carried out on separation and catalytic conversion processes and it comprises analytical equipment. Separation processes include adsorption and liquid-liquid extraction which are being applied for removing organic sulfur compounds from petroleum fractions i.e. they are being used as adsorptive and extractive desulfurization processes. Catalytic conversion process that is being investigated is isomerization of light n-alkanes which produces isomers with much higher octane number values. The research of these processes is being conducted on laboratory apparatuses which were conceived and designed at the Petroleum and Petrochemistry Department and built in cooperation with Lab Air Media d.o.o. company from Sisak.

During the time it took to complete the Laboratory the research that was carried out resulted with one completed Ph.D. thesis and the work on three more is ongoing. Also, 8 scientific papers were published in journals indexed in Current Contents and 2 are near completion, and additional 14 other scientific papers were published.

Investigated processes and equipment

Adsorptive desulfurization

Adsorption is a process during which the molecules of the adsorbate are being accumulated on the boundary area between solid surface and a fluid (liquid or gas) in the concentration larger than the concentration of the adsorbate in the liquid or gas. Adsorption can be used for desulfurization based on the ability of a specific adsorbent to selectively adsorb organic sulfur compounds from petroleum and its fractions. The research of adsorption is being carried out by batch experiments in vessels as adsorbers and continuous experiments in fixed bed columns. Accordingly, the batch and column adsorptive desulfurization apparatuses were developed and built in the Laboratory. Batch adsorption experiments are being carried out in order to determine equilibrium relations and to test the effectiveness, i.e. screen out commercially available adsorbents and determine the one with the best properties in regard to the ability to remove organic sulfur compounds. The column adsorption experiments are being carried out in order to approximate the conditions at which this process would be carried out in practice and the process modeling based on these results enables it's simulation and scale-up calculations. Batch adsorptive desulfurization apparatus is shown on Figure 1. Adsorption is carried out in 250 cm^3 stainless steel vessels as adsorbers at atmospheric pressure and temperatures from 20 to 80 °C. Special feature of this apparatus is the innovative adsorbent dozing system comprising an electric valve with piston and a funnel. The apparatus is controlled by the computer which significantly simplifies handling and operation and improves repeatability the experimental results.

Continuous adsorptive desulfurization in a fixed bed column is being carried out in the column adsorption apparatus shown on Figure 2. Apparatus enables precise process control and measurement of process variables including temperature, flow rate and time, and can carry out automatic sampling according to the preset values of sample volume and time.

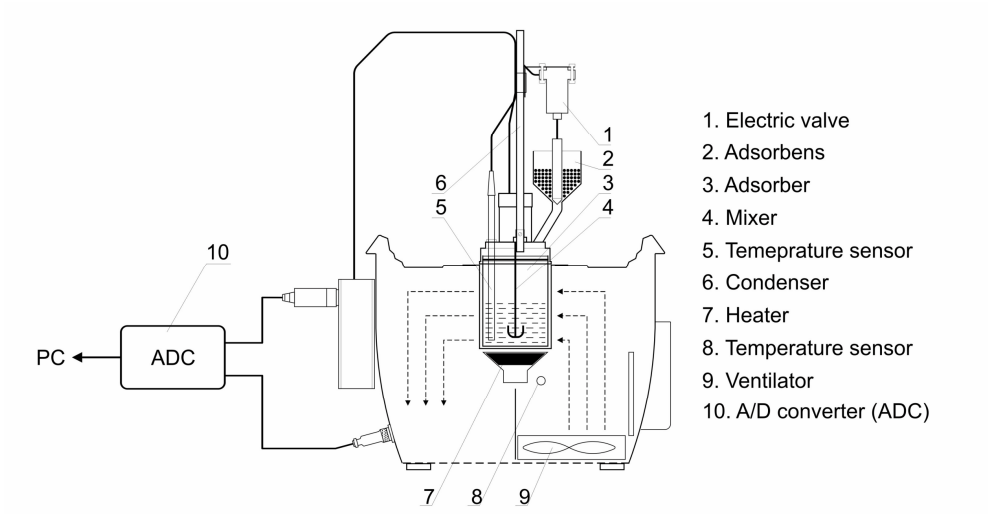
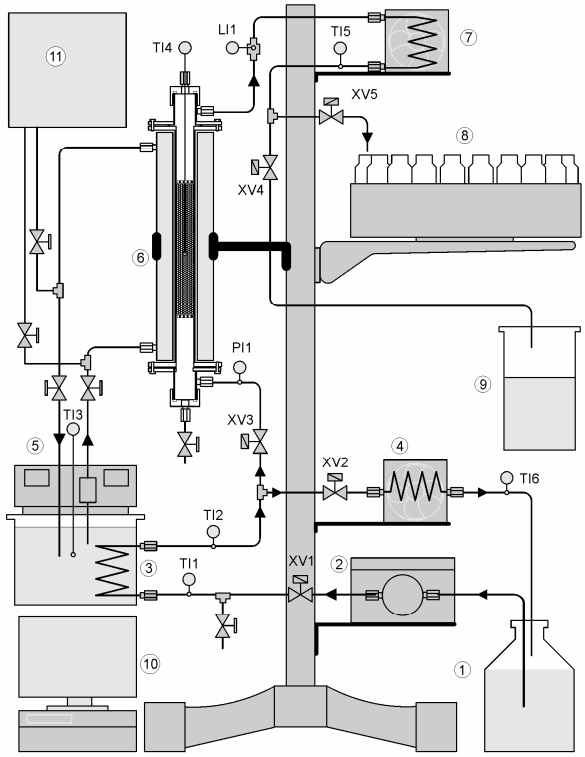


Figure 1. Batch adsorption apparatus

Process is conducted in a stainless steel column with internal diameter of 2,2 cm and total length of 28,4 cm, and three different bed depths can be set. Apparatus is controlled by a software process controller through the corresponding interface. The driver program enables the automation of the apparatus and maximal flexibility in regard to possible malfunction or other process disturbance and/or stoppage. Data acquisition is carried out according to the preset conditions. The software interface is divided in to several units that allow the setting of process variables (working temperature, feed flow rate and sampling program), process control, timer and the total feed volume. The feed flow rate is digitally controlled using a pump with the range between 0,01 and 30,00 $cm^3\,min^{-1}$. The temperature is regulated in the range between 5 and 80 °C. The working temperatures of below 20 °C and down to 5 °C are achieved by a compressor water cooler while the temperature up to 80 °C are achieved by a heating water bath. The automatic sampling of up to 20 samples can be programmed via the software interface by setting the volume of the sample, the number of the samples and the sampling interval, i.e. the volume of the treated feed that pass between to sampling sequences. The condition that needs to be satisfied in order to enable the automatic sampling is the indication that the column is full and the treated feed started coming out of the column and for this reason a completely new light sensor was developed and used. In the case of any process malfunction or delay the feed flow is automatically switched to circulation.

The acquisition of the data were enabled in three ways and in normal procedure is activated according to sample list. The data is stored in text file format. The software interface schematic displays the indicators showing the state of different apparatus units and flow lines and separate windows with measured values of temperature, pressure and flow rate as well as sensor states.

The level of the liquid in the feed tank is calculated from the set value of the total added feed volume and is numerically and visually displayed on the software interface which also contains a graphical display of the state of three process variables in real time.



1 Feed tank
2 Pump
3 Preheater
4 Circulation air cooler
5 Water bath
6 Adsorption column
7 Product air cooler
8 Auto-sempler
9 Product tank
10 Process controler
11 Cooling system
TI1 Temperature of the feed
TI2 Temperature of the feed after preheater
TI3 Temperature of the water bath
TI4 Tmperature in the column
TI5 Temperature of the product after air cooler
TI6 Temperature of the feed

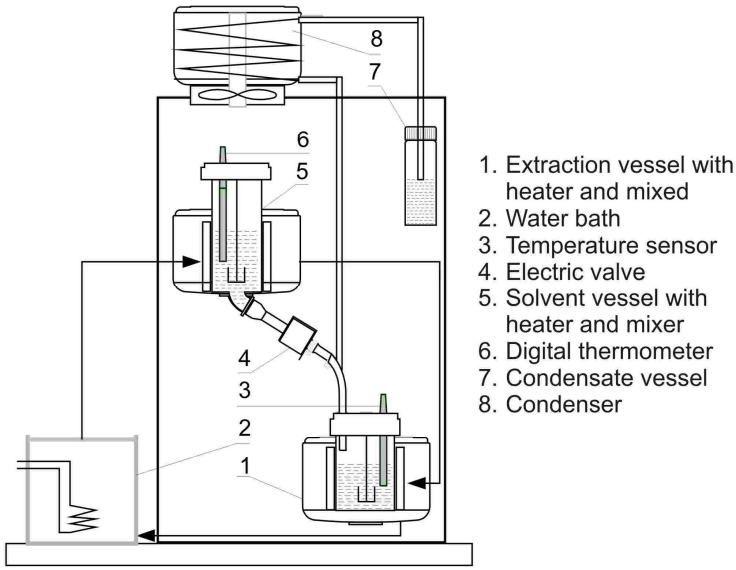
Figure 2. Column adsorption apparatus

Extractive desulfurization

Extraction can be used as a desulfurization process based on the difference in solubility of organic sulfur compounds in petroleum fractions and in a solvent which are not mixable. Liquid extraction is a diffusion process during which one or more components are transported from one liquid phase to the other liquid phase with the goal of achieving selective removal of these components. The investigation of the extraction process is carried out, as in the case of adsorption, in batch and column experiments.

Apparatus for batch extraction is shown on Figure 3 and the main parts are the vessels for the solvent and the feed, the so called extractor with a mixer and temperature sensor, water bath, heat exchangers and an electric valve.

Experiments can be conducted in temperature range between 20 and 90 °C. The extractor mixer rotation speed can be regulated in the range between 100 and 700 rpm. The solvent and extractor vessels are connected by an electric valve which opens when the preset working conditions are reached and the process starts. The conditioning and the process control are conducted by the computer and specifically developed software.



Figue 3. Apparatus for batch extraction

To facilitate the conduction of extractive desulfurization in conditions as similar as possible to the industrial process, an apparatus for continuous column extraction was developed and built (Figure 4). The apparatus, besides the fact that can be used for investigating industry like extraction process, is suitable for the training of students. The main units of the apparatus are the extraction unit, the vacuum distillation unit and the rafinate washing unit. The extraction unit comprises a 1000 mm long glass column with internal diameter of 30 mm within which a vertical mixer with perforated plates is installed. The vertical mixing speed of the mixer can be regulated. The feed and the solvent are introduced in to the column by two pumps with adjustable pumping range between 10 and 300 cm^3 min^{-1}. The flow lines are heated before the column and cooled with air coolers after the column and before the tanks. The handling of the liquids during operation is alleviated by the additional pumps which are used for emptying parts of the apparatus into, so called, slop vessels. The vacuum distillation unit facilitates the regeneration of the solvent and its repeated use and the main parts are vacuum pump, heater of the distillation flask and coolers.

The rafinate washing unit is used in experiments when sulfolane is used as the solvent in order to remove the residual sulfolane from the product and it comprises systems for charging and emptying, a mixer and a glass washing vessel. The apparatus is controlled by the process control software which enables precise regulation and measurement of process variables and it has an integrated video system for taking pictures of liquid bubbles that form during operation.

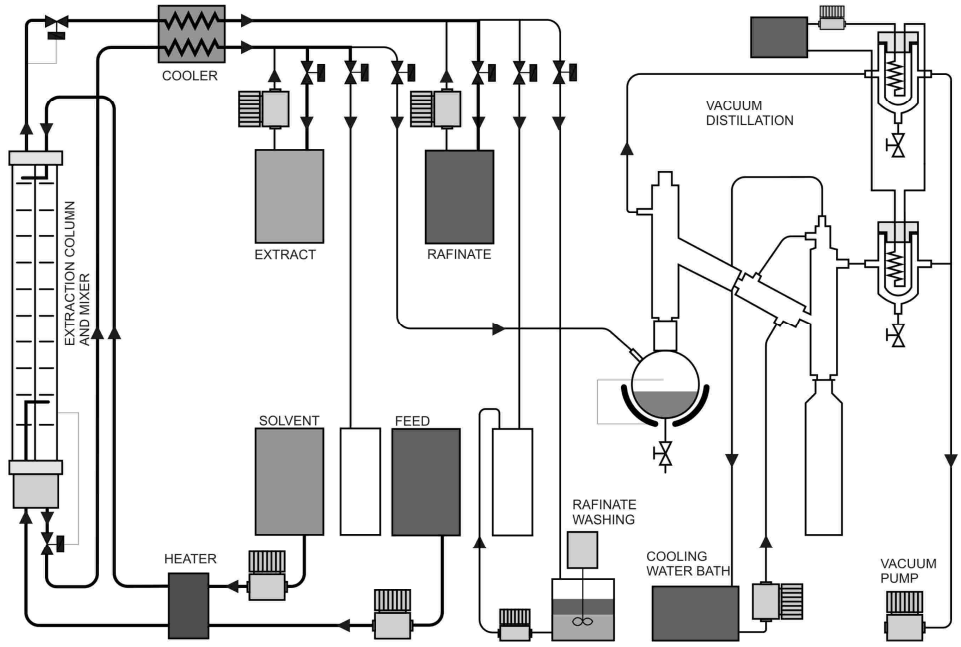


Figure 4. Apparatus for column extraction

Isomerization

Isomerization in the Petroleum and Petrochemical Process Engineering Laboratory is being investigated as the process for compensation of octane number loss in gasoline due to the lower permitted aromatic content, the greater severity of hydrodesulfurization and the restrictions in use of additives.

Figure 5 shows the schematic of the apparatus for the catalytic conversion processes which is used for isomerization and depending on the type of catalyst can be used for hydrogenation and hydrodesulfurization of lighter petroleum fractions. The main parts of the apparatus include feed system, pre-heater, reactor system and high pressure separator. Additional key components include slop vessel, product vessel, cooling system and the process control unit comprising software, interface and controllers.

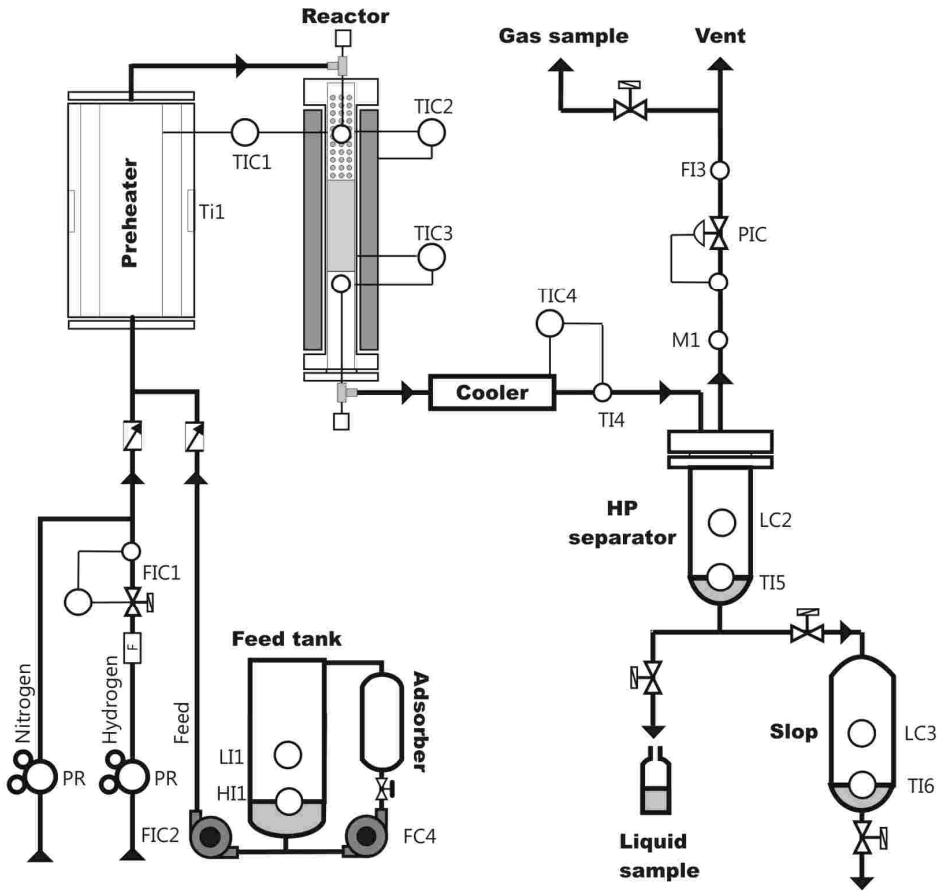


Figure 5. Apparatus for catalytic conversion processes

The feed system comprises a two liter tank with liquid level control, pump with pumping range between 20 and 200 cm^3min^{-1} and ability to achieve pressures up to 40 bars and a sub-system for drying when the feed is real light gasoline. Drying is carried out using an additional pump to transport the feed trough a fixed bed adsorption column filled with appropriate adsorbent which is in this case silicagel. The moisture content measurement is carried out by a HMT type sensor in the range between 0 and 1000 $mgkg^{-1}$. The feed is introduced into the hydrogen stream before it enters the reactor system and this mixture is pre-heated in order to achieve better regulation and control of temperature during processing. Pre-heater comprises a spiral stainless steel pipe in an aluminum block with heaters.

Pre-heated feed and hydrogen enter the tubular reactor that has a total volume of 61,5 cm^3 which contains a fixed bed of up to 20 cm^3. The space between the entrance to the reactor and the fixed bed is filled with glass balls facilitating additional pre-heating and better heat distribution as well as better matter distribution. The reactor, along its axis, is encompassed by two heaters controlled by PID controllers – the first for additional pre-heating control and the second for temperature control of the fixed bed. After the mixture of products and un-reacted feed exits the reactor it is cooled and it enters the high pressure separator. High pressure separator has a total volume of 350 cm^3 and has an integrated liquid level control system. The gas phase consisting mainly of hydrogen is released into the atmosphere by way of pressure regulator and a ventilation system while the liquid phase is accumulated up to a preset level. The liquid level control in the separator facilitates sampling without disrupting the pressure level in the apparatus.

The process control software has the ability to measure and regulate 16 process variables hence comprising 16 analogue outs used for controlling valves, sensor reading and data logging. Software interface enables real time graphical monitoring of up to 6 process variables of choice. During operation three software counters measure the total volumes of hydrogen and feed that pass through the apparatus in one catalysts life cycle.

Analytics

Analytic methods present in the Laboratory include gas chromatography, wave dispersive x-ray fluorescent spectrometry and UV-VIS spectrometry. Gas chromatograph is a Shimadzu GC-2014 with two flame ionization detectors (FID) and a Phenomenex Zebron ZB-1 capillary column meant for the analysis of hydrocarbon compounds with 1 to 12 C atoms. Wave dispersive x-ray fluorescent spectrometer is a PANalytical Venus 200 MiniLab with scandium 200 W x-ray tube. This device is used for elementary analysis of solids, powders and organic solutions. The exposition of the sample to the x-ray radiation from an outside source causes it to radiate secondary x-ray radiation or primary fluorescent radiation which is specific for each element, although some compounding is possible. By adjusting the angle of the detector or by directing the fluorescent radiation at a certain angle to the fixed detector the presence of a particular element emanating the fluorescent radiation can be detected and by measuring the intensity of the radiation the quantity of element san be determined. UV-VIS spectrometer is a PerkinElmer Lambda 16 which is used for determination of colored compounds in liquid samples and in this Laboratory is being used in the refining waste water treatment experiments.

References

1. http://bib.irb.hr/
2. Gomzi Z., Kemijski reaktori, HINUS, Zagreb, 1998.
3. Cooney D. O., Adsorption desing for wastewater treatment, CRC Press, Boca Raton, 1999.
4. Mužic M., Napredni procesi desulfurizacije naftnih frakcija, Disertacija, FKIT, Zagreb, 2009.
5. Sertić-Bionda K., Janović Z., Gomzi Z., Mužic M., Adžamić T., Zoretić Z., Odsumporavanje FCC benzina kapljevinskom ekstrakcijom 2, Elaborat, FKIT, Zagreb, 2007.
6. Sertić-Bionda K., Adžamić T., Mužic M., Glasnović A., Sander A., Zoretić Z., Odsumporavanje FCC benzina kapljevinskom ekstrakcijom 5, Elaborat, FKIT, Zagreb, 2009.
7. Janović Z., Naftni i petrokemijski procesi i proizvodi, GOMA, Zagreb, 2005.
8. Sertić-Bionda K., Gomzi Z., Adžamić T., Mužic M., Marčec-Rahelić N., Adžamić Z., Optimiranje izomerizacije lakog benzina 5, Elaborat, FKIT, Zagreb, 2009.
9. Brouwer P., Theory of XRF, PANalytical B.V., Almelo, 2006.

Authors
dr. sc. Marko Mužic
prof. dr. sc. Katica Sertić-Bionda
Faculty of Chemical Engineering and Technology, Univerity of Zagreb
mmuzic@fkit.hr