

E2KW 2014

Proceedings of the
Energy and Environment
Knowledge Week 2014

Toledo, Spain
30th-31st – October



Proceedings of the
**Energy and Environment
Knowledge Week 2014**
(E2KW2014)

Edited by:

Francisco José Sáez-Martínez, Elena Jiménez Martínez,

Luis Sánchez Rodríguez

Gilles Lefebvre, José Mondéjar Jiménez and Francisco Javier

Tapiador Fuentes

ISBN: 978-84-697-1162-0

2014



OCTANE UPGRADING OF GASOLINE BY ABSORPTION PROCESSES

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OCTANE UPGRADING OF GASOLINE BY ABSORPTION PROCESSES

1. Purpose

Along the last decades, the refining industry has attempted to enhance the octane quality of the gasoline fulfilling the environmental standards imposed. This continuous effort began in 1970, when Shell started the first hydroisomerization reactor, the Hysomer, whose function is to convert the low RON (RON – Research Octane Number) linear paraffins into high RON branched ones by catalytic reaction at a temperature range between 500 K and 550 K. However, this reaction is incomplete and a large fraction of linear molecules remain in the output isomerate. To overcome this problem, Universal Oil Products -UOP coupled to this reactor an adsorption unit, named IsoSiv, packed with zeolite 5A. This unit removes the normal paraffins from the output of the catalytic reactor, and recycles this stream for complete conversion in the Hysomer. The resulting cluster is known as the Total Isomerization Process –TIP and the octane enhancement results in an isomerate having RON of 82. The art has produced several improvements to the first process, based upon the discovery that considerable improvements can be achieved in terms of improved energy efficiency. By the same time the Institute Français du Pétrole - IFP, proposed a novel process by combining the high activity system using a new catalyst, and at the same time improving the desorption of n-paraffins combining pressure drop and a stripping operation using an isopentane rich vapour. However, the data from reveal that 30% of the typical composition of the final product consists of low RON mono-branched C6 isomers, with implications in the RON number of the final product. In practice, it is necessary to separate the low RON mono-branched isomers from final product and recycle then to the isomerization reactor. This separation is not an easy task because the molecular sieving effect observed with 5A zeolite to separate linear from branched paraffins will not work.

2. Design, Methodology or Approach

In this work we studied the separation linear/mono/di-branched paraffins in a cyclic Pressure Swing Adsorption process using a layered bed of zeolites 5A and Beta (Figure 1). Zeolite Beta proved to be an efficient separator of mono-branched from di-branched paraffins. Aspen ADSIM (AspenTech Inc.) was used for numerically solve an adiabatic dynamic model incorporating mass, energy and momentum balances. Model parameters were taken from experimental data obtained in our lab. The studies were performed with the objective to determine how process performance is affected by purge quantity, 5A-to-Beta ratio, repressurization/blowdown schemes and operating temperature which are typical operating parameters of PSA processes.

3. Results/Findings

Figure 2 shows the product average RON as a function of the zeolite 5A layer length and purge-to-feed ratio at $T = 523$ K, where it can be seen that RON is above 90 when the ratio of the layered bed is nearly 0.6. It was also demonstrated that a slight increase in temperature (20 K) results in a RON benefit of 0.2 points. Several alternatives are also provided to improve the performance of the existing TIP processes with this combination of adsorbents.

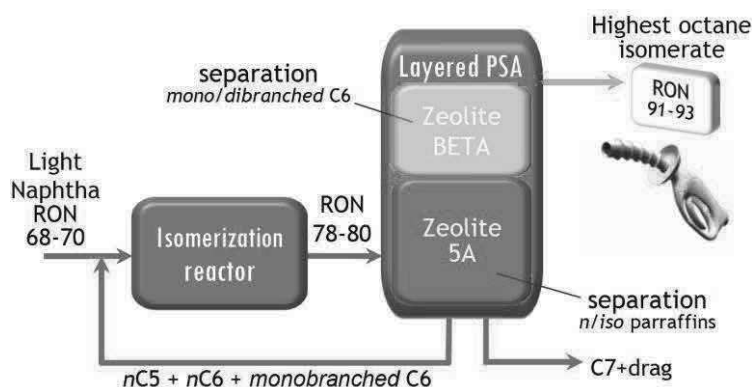


Figure 1. Improvement of the TIP processes in a layered PSA.

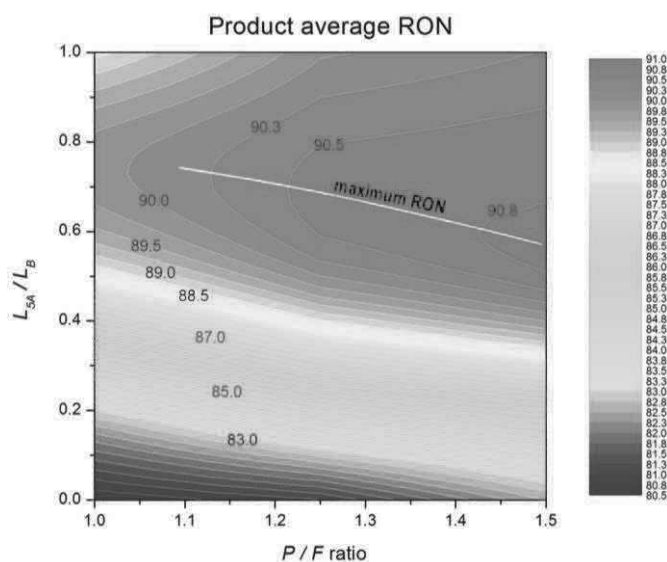


Figure 2. Product average RON as a function of the zeolite 5A/BETA layer ratio (L_{5A}/L_B) and purge-to-feed (P/F) ratio at $T = 523$ K and $t_{press}/t_{feed} = 20/80$ s.

4. Conclusions

The performance of a layered pressure swing adsorption (PSA) process for the separation of high research octane number (HRON) paraffins from a C_5/C_6 light naphtha fraction is simulated with a detailed, adiabatic single column PSA model. A zeolite 5A layer is used for selective adsorption of the low RON linear paraffins while a zeolite beta layer is used to separate the intermediate RON 3MP from the HRON fraction.

It is demonstrated that an optimal zeolite 5A-to-zeolite beta ratio can improve the product average RON up to 1.0 point compared to actual existing TIP processes using zeolite 5A only. Moreover, process simulations demonstrated that increasing the operating temperature from 523 K to 543 K results in an octane gain of 0.2 RON.