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Separation of Light Naptha by Adsorption Processes

Patrick S. Bárcia^a, Alírio E. Rodrigues,^b and José A.C. Silva^{*,a}

^aLaboratory of Separation and Reaction Engineering, Escola Superior de Tecnologia e Gestão, Instituto Politécnico de Bragança, Apartado 134, 5301-857 Bragança, Portugal

^bLaboratory of Separation and Reaction Engineering, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua do Dr. Roberto Frias, S/N 4200-465 Porto, Portugal

*Corresponding author, email: jsilva@ipb.pt

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 (Holcombe (UOP) [1]), 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, Minkinnen (IFP) [2] 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 (Holcombe [1], Minkinnen [2]) 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.

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 [3]. 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. 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 [4].

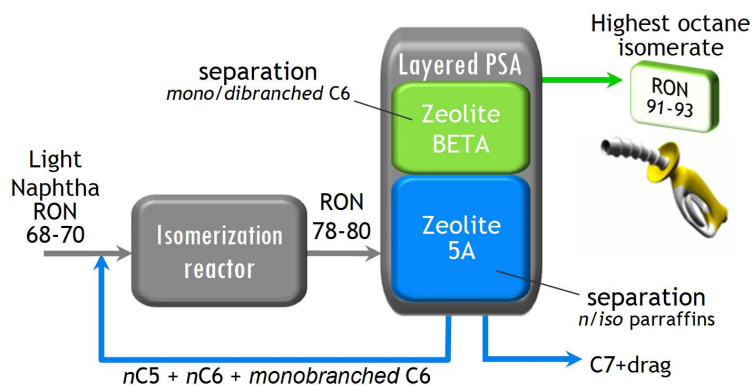


Figure 1. Improvement of the TIP processes in a layered PSA.

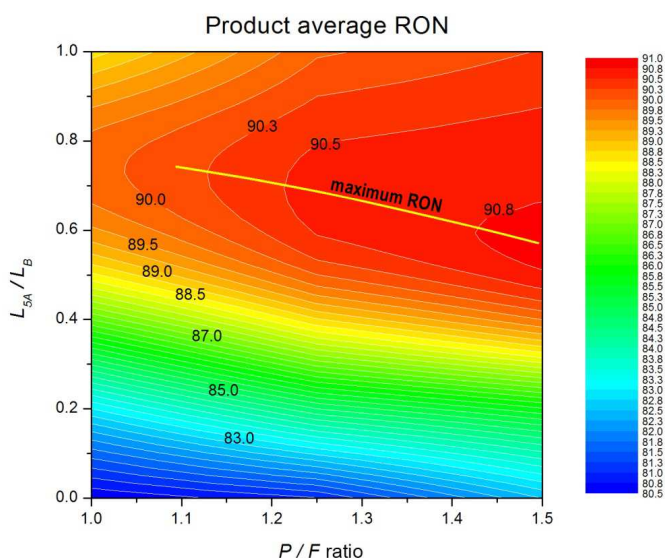


Figure 2. Product average RON as a function of the zeolite 5A/BETA layer ratio (L_{5A}/L_B) and purge-to-feed (P/F) ratio at $T = 523$ K and $t_{press}/t_{feed} = 20/80$ s.

References:

- [1] T. C. Holcombe, T. C. Sager, W. K. Volles, A. Zarchy, Isomerization Process U.S. Patent, 4,929,799, 1980.
- [2] A. Minkinen, L. Mank, S. Jullian, Process for the isomerization of C5/C6 normal paraffins with recycling of normal, U. S. Patent, 5,233,120, 1993.
- [3] P. S. Barcia, J.A.C. Silva, A. E. Rodrigues, Multicomponent Sorption of Hexane Isomers in Zeolite BETA, AIChE J. 53 (2007) 1970-1981.
- [4] P. S. Barcia, J.A.C. Silva, Alario E. Rodrigues, Octane Upgrading of C5/C6 Light Naphtha by Layered Pressure Swing Adsorption, Energy Fuels, 2010, 24, 5116-5130.