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REACTOR TEMPERATURE OPTIMIZATION OF THE LIGHT NAPHTHA ISOMERIZATION UNIT

Abstract

Isomerate, the product of an Isomerization unit, is a high octane number gasoline blending component characterized by low (or none at all) aromatic and sulfur content which also satisfies both economic and ecological demands. Quality of the isomerate is affected by a number of parameters, such as feed composition, process parameters, process engineer attention to daily operation, etc. Some process parameters are set by the design basis or production planning while some others, like reactor temperatures, are optimized by a process engineer. During the optimization, reactor outlet temperatures are adjusted in the lead and lag reactors to maximize the reaction rate in the lead reactor and to manipulate the equilibrium concentrations in the lag reactor. This combination will maximize desired component product ratio, the so-called iso-ratio. The optimum can be chosen out of two options: to produce maximum isomerate barrels (maximum liquid yield) or to produce maximum product octane number. This paper deals with reactor temperature optimization background and results. The optimum inlet start-of-run temperature for the lead reactor was set to 117 °C and for the lag reactor around 120 °C.

1. Introduction

In January 2012 the new Light Naphtha Isomerization unit was started up in the Sisak Refinery. The unit is designed for the continuous catalytic isomerization of pentanes, hexanes, and mixtures thereof.[1] The reactions take place in a hydrogen atmosphere, over a fixed bed of catalyst, and at operating conditions which promote isomerization and minimize hydrocracking.[2] The major elements of the Unit are the deisopentanizer column (DIP), liquid feed and makeup gas driers, the Penex reactors (lead and lag), the product stabilizer, the caustic scrubber and the deisohexanizer column (DIH), as illustrated in Figures 1 and 2. The design data represent a base for calculations in order to ensure efficient operation of the unit. But, it was necessary to further optimize reactors operation and catalyst activity in respect of real feed processed in the unit.

The Isomerization unit product (isomerate) quality is affected by several factors, like feed composition, process parameters, focus of process engineers on the everyday

unit operation, etc. While some process parameters are set by the design basis or production/planning department, others, like reactor temperatures, can be optimized by a Penex process engineer. If the reactor temperatures are not adjusted in correlation with feed composition and process parameters, the product octane number decreases below maximum achievable value, which represents insufficient utilization of the unit, worse product qualities and direct financial loss.

Since the isomerization reaction is an equilibrium reaction, equilibrium of iso- and normal paraffins will be reached at the reactor effluent. When this equilibrium is reached, maximum product ratio or equilibrium product ratio will be obtained. Any attempt to exceed equilibrium product ratio with the idea of producing more iso-paraffins in the reactor effluent would only result in less iso-paraffin yield and an increase in propane and lighter yield due to hydrocracking.[1] Process parameters, at which an equilibrium of iso- and normal paraffins reached at the reactor effluent is close to theoretical values, are defined by optimization of the reactor temperatures. This equilibrium represents maximum achievable Penex product quality.

2. Experimental part

2.1. Isomerization process

The DIP-Penex-DIH system of the Sisak Refinery Light Naphtha Isomerization Unit is illustrated in Figure 1. The unit produces the highest octane product and highest product yields if compared with other UOP technologies for light naphtha isomerization.[3]

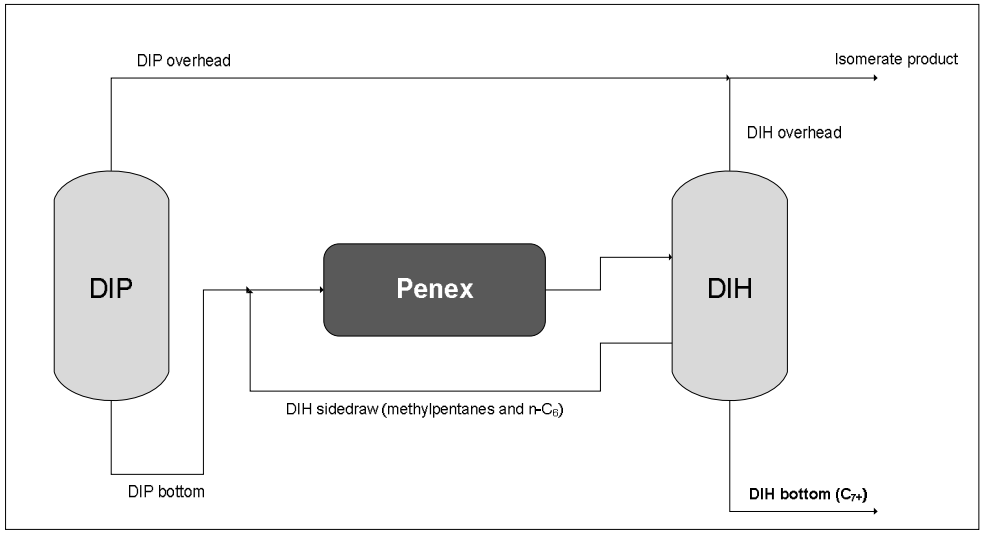

Figure 1: UOP DIP-Penex-DIH system for high octane isomerate production

The Isomerization unit feed is a mixture of two streams: hydrotreated light naphtha, from the hydrotreating unit, and light reformate, from the Deheptanizer (DH) column. Isomerization of light naphtha takes place in the Penex section and octane number is increased by transformation of linear C5/C6 hydrocarbons into the branched ones. High octane isopentanes are separated from normal paraffins, hexanes and C7+ hydrocarbons in the DIP column. The Penex reactors are loaded with a platinum based catalyst where the isomerization reactions take place. The Penex section is illustrated in Figure 2.

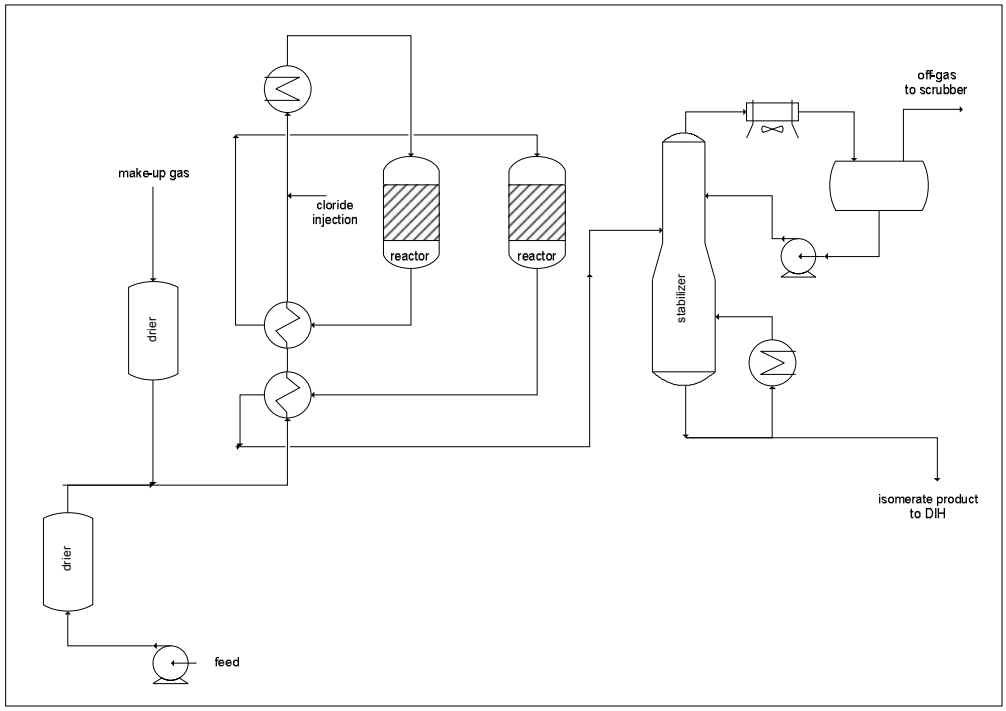

Figure 2: Simplified scheme of the Penex section of the light naphtha isomerization unit

Prior to the entry of the combined liquid hydrocarbons and hydrogen rich gas stream into the charge heater and the lead/lag reactors, both feed streams are dried in liquid and make-up gas driers. The purpose of the liquid and gas feed driers is to eliminate oxygenated compounds which permanently deactivate catalyst.[1] After the combined feed is heated up to the reactor temperatures, it flows to the lead and lag Penex reactors that are operated in series. Downstream the feed/reactor effluent heat exchangers and upstream the charge heater, organic chlorides are injected in order to maintain acid function of the catalyst. After exiting the lag reactor, the product stream is cooled in heat exchangers and is then routed to the stabilizer for

separation of light hydrocarbons from liquid stream. Chlorides are scrubbed from the light hydrocarbons in the scrubber by caustic solution. The stabilizer bottom is routed to the DIH column where the highly valuable isohexanes and C5 compounds are separated as a top product, while methylpentanes, n-hexane and part of C6 cyclics are recycled back to the lead reactor providing the high product octane. The bottom product contains the rest of C6 cyclics and C7+ hydrocarbons. The Isomerization product, isomerate, which is a mixture of the DIP and DIH overheads, is mainly composed of high octane compounds like isopentane, 2,2-dimethylbutane and 2,3-dimethylbutane.

2.2. Reactor temperature optimization

During the optimization, the reactor outlet temperatures are adjusted in the lead and lag reactors to maximize the reaction rate in the lead reactor and to manipulate the equilibrium concentrations in the lag reactor.[2] This combination will maximize the desired product iso-ratio for achieving economic optimum which can be to produce the maximum isomerate octane-barrels (maximum liquid yield) or to produce a maximum product octane. Due to regulations reducing the allowable benzene content of the total gasoline pool[4] some refiners require increase of the benzene and reformer benzene precursors (methylcyclopentane and cyclohexane) in the Penex feed which leads to maximizing liquid yield. In that way, without a high octane requirement in isomerate, the benzene content is decreased in reformate and the gasoline pool. However, other refiners prefer maximization of the product octane and choose to sacrifice some liquid yield.

The iso-ratio is the weight percentage of the particular paraffin divided by the total weight percentage of all isomers of that paraffin.[3] It is a common measure of how close a product or feed stream is to the equilibrium composition in given process conditions.[3] Octane number of isopentane, 2,2-dimethylbutane and 2,3-dimethyl-butane is 93.5, 94.0 and 105.0, respectively. By monitoring their iso-ratios it is possible to control performance of the reactor section. For each component in the system, there is an equilibrium concentration that is permitted by thermodynamic principles and it is relatively easy to track how close to equilibrium the reactors operate. Figure 3, below, illustrates a plot of vapor and liquid equilibrium values versus temperature for the ratio of isopentane to all C5 paraffins (iC5/C5P iso-ratio). The equilibrium values are primarily a function of temperature and phase (liquid or vapor) and are not dependent upon feed composition.[2] As an example, at 150 °C and all vapor phase reactions, the iC5/C5P ratio is 77,2% on either a weight or mole basis (all paraffin pentanes will have the same molecular weight). Thus, if a pure sample of n-pentane were placed in a reactor at these conditions with a theoretically perfect catalyst, and for an infinite amount of time, the product would contain 77.2% iC5 and 22.8% nC5. It would be impossible for the product to contain a higher amount of iC5 no matter how good the catalyst is. This is a fixed value based upon thermodynamic principles. As in iC5/C5P case, the 2,2-DMB/C6P ratio is favored at lower temperatures. If the reactor outlet temperature is 140-170 °C, the iso-ratio is

25-35%. The 2,3-DMB/C6P product ratio should always be ~10.5 wt% as the equilibrium value is constant for all Penex reactor temperatures.[2]

Among process parameters of the isomerization unit, the pressure, space velocity, and feedstock composition are typically set by the design basis and/or the production/planning department. The hydrogen to hydrocarbon ratio should always be maintained in excess of 0.05 moles of hydrogen (at reactor outlet) per mole of hydrocarbon charge to allow the reactions to proceed to completion.[1] Since there is no noticeable advantage in adjusting the hydrogen to hydrocarbon ratio to increase the product octane, the reactor temperatures are the only significant, adjustable parameter used to optimize the reactor's performance for different feedstocks and charge rates to the Penex Unit.[2]

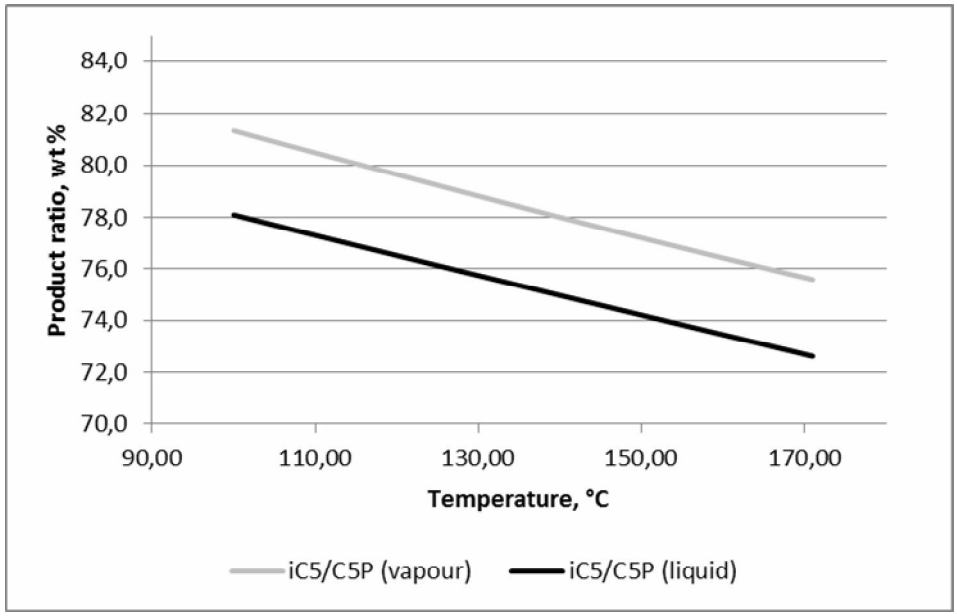

Figure 3: Equilibrium iC5/C5P ratios in vapor and liquid phase[2]

Some key components in the Penex reactor charge that effect catalyst performance are the C6 cyclics and C7+ compounds which are, for simplicity, combined into an X factor. The key product ratios (measured in the lead reactor effluent and the stabilizer bottoms) are iC5/C5P, 2,2-DMB/C6P, and 2,3-DMB/C6P. The sum of these three product ratios is referred to as the paraffin isomerization number (PIN).[1] For an increase in feed X factor of 1 number, a decrease in product PIN can typically be expected in the range of 0.5 numbers due to a tendency of the C6 cyclics and C7+ components to absorb into the catalyst, covering the active sites.[2] In order to compensate for the loss of active sites, higher temperatures will be required to reach the optimum performance of the catalyst.

Increases in the space velocity will also require higher reactor temperatures for a maximized product PIN and related octane. Conversely, decrease in the space velocity will require lower reactor temperatures for a maximized PIN and related octane.[2] Since the reactions are limited by equilibrium, it is necessary to use the reactor outlet temperature rather than the reactor inlet temperature to optimize. The inlet temperature is controlled and used to achieve the desired reactor outlet temperature. An average operating space velocity and X factor should be maintained during a temperature optimization exercise. If the operating space velocity and X factor routinely change significantly above and below the average values identified in the base optimization then it is recommended that an additional higher and lower optimization be completed at the variable's extremes to account for these variations. The unit can then be maintained close to its optimum the majority of the time by interpolation of the optimum reactor outlet temperatures between the variable's extremes.

Before starting the reactor temperature optimization it is necessary to select the desired overall space velocity (LHSV) and feedstock composition for optimization. Two to three days of operation on a similar feedstock are desired. For the baseline compositional data it is necessary to sample the reactor charge, lead reactor effluent, and stabilizer bottoms. Throughout the optimization process, the same overall space velocity is being recorded and maintained, as well as hydrogen to hydrocarbon ratio and reactor pressure. The reactor outlet temperatures must be recorded along with the results of lab analysis for iC5/C5P, 2,2-DMB/C6P and 2,3-DMB/C6P product ratios from the lead and lag reactors.

Optimization of lead reactor temperatures is first carried out. The lead reactor outlet temperature is increased in 3-5 °C increments. After all the lead reactor temperatures have stabilized for at least two hours, a lead reactor effluent sample is taken. After the action is repeated several times at different reactor temperatures, the lead reactor outlet temperature should be returned to the original baseline value and the reactor charge should be sampled again. Once laboratory data is available, it is necessary to plot the iC5/C5P, 2,2-DMB/C6P and 2,3-DMB/C6P product ratios and the vapor/liquid equilibrium values at the varying reactor temperatures. The lead reactor outlet temperature should then be set at the temperature that provided the highest iC5/C5P product ratio.

After the optimization of the lead reactor temperatures is finished, the optimization of the lag reactor temperatures is carried out in the same way as for the lead reactor. Before sampling the stabilizer bottoms, it is necessary to wait four hours after the lag reactor temperatures stabilize following temperature adjustments. A total of four or five samples of the stabilizer bottoms should be taken over the course of the lag reactor optimization. After all the samples are taken, it is necessary to return the lag outlet temperature to the baseline value. Once laboratory data is available, it is necessary to plot the iC5/C5P, 2,2-DMB/C6P and 2,3-DMB/C6P product ratios and the vapor/liquid equilibrium values at the varying reactor temperatures.

The initial reactor temperature optimization was performed 23-26 January during first start-up of the Light Naphtha Isomerization Unit in Sisak Refinery at 80-89% of design capacity. Process parameters maintained during optimization are shown in Table 1. The lag reactor pressure was maintained at 31,4 bar, and the hydrogen to hydrocarbon ratio above 0.05 mol %. As the performance of the light naphtha isomerization unit is affected by the content of compounds other than C5/C6 paraffins, like feed benzene, cyclic C6 and C7+, the presence of these compounds is monitored as a sum of their weight content, expressed as X factor.

Table 1: Process parameters during reactor temperature optimization

reactor	X factor	LHSV	hydrogen to hydrocarbon ratio
lead	4.5	1.23 h^{-1}	0.11-0.07
lag	4.3	1.33 h^{-1}	0.07

3. Results and discussion

The reactor temperature optimization was performed at 80-89% of the unit design capacity. The LHSV was maintained at 1.23 h^{-1} for the lead reactor, and 1.33 h^{-1} for the lag reactor. The X factor, an indicator of undesired compounds presence, was 4.5 for the lead reactor, and 4.3 for the lag reactor. The hydrogen to hydrocarbon molar ratio was above 0.05.

As the 2,3-DMB/C6P product ratio is always ~10.5 wt% for all Penex reactor temperatures, the ratio is not represented in this paper.

a) Lead reactor optimization

The inlet temperatures were set and stabilized for about two hours prior to taking a sample. The results of the lead reactor optimization are shown in Table 2 and illustrated in Figures 4 and 5.

Table 2: Lead reactor optimization results

reactor inlet temperature, °C	reactor outlet temperature, °C	iC5/C5P ratio	2,2-DMB/C6P ratio
118.7	145.8	75.4	29.3
121.3	146.6	75.0	28.7
125.3	154.6	74.9	28.5
129.3	157.8	74.6	28.0
133.8	161.7	74.5	27.8

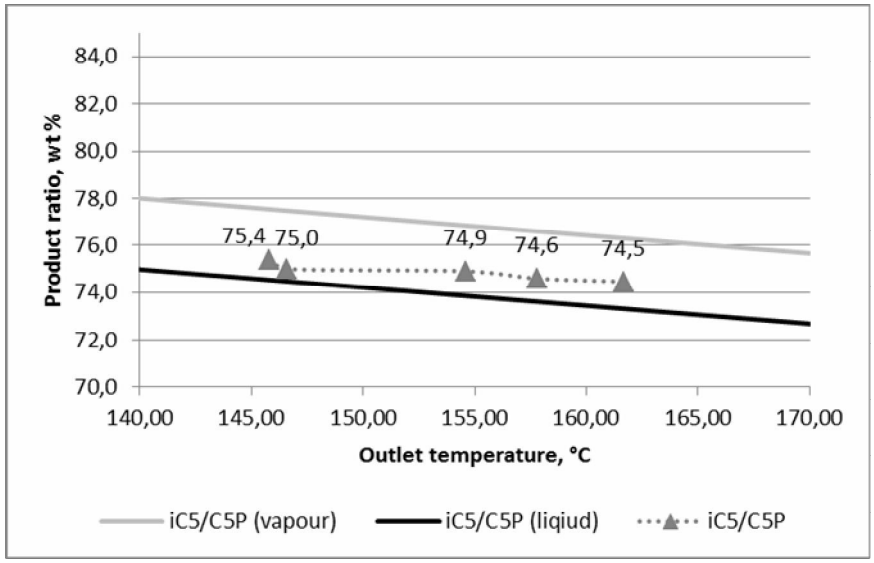

Figure 4: iC5/C5P product ratio in the lead reactor during optimization (LHSV = 1.23 h^{-1}; X = 4.5)

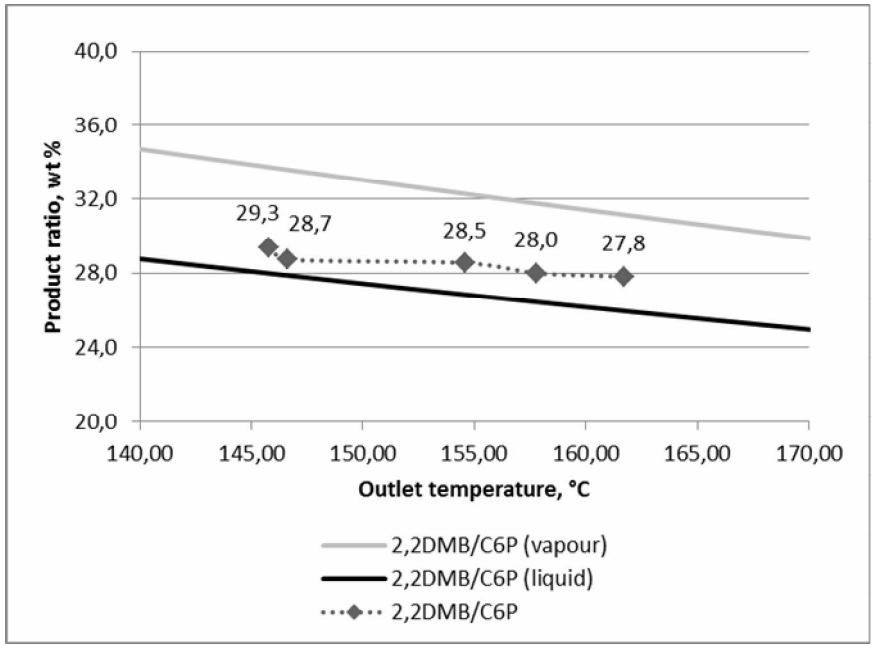

Figure 5: 2,2-DMB/C6P product ratio in the lead reactor during optimization (LHSV = 1.23 h^{-1}; X = 4.5)

The results show that the highest iC5/C5P (75.4%) and 2,2-DMB/C6P (29.3%) ratios were reached at the reactor outlet temperature of 145.8 °C. The corresponding reactor inlet temperature was 118.7 °C. The lowest iC5/C5P and 2,2-DMB/C6P ratios were found at the reactor outlet temperature of 161.7 °C. The corresponding reactor inlet temperature was 133.8 °C. In conditions with a reactor outlet temperature being higher than that required for maximum isomerization, the product ratios and liquid yield will decrease due to increase in hydrocracking reactions.[2] It was found that the optimum reactor outlet temperature was 145 °C, which corresponded to a reactor inlet temperature of 118.7 °C. The optimum inlet start-of-run temperature for the lead reactor was set on 117 °C.[4]

b) Lag reactor optimization

The inlet temperatures were set and stabilized for about two hours prior to taking a sample. The results of the lag reactor optimization are shown in Table 3 and illustrated in Figures 6 and 7.

Table 3: Lag reactor optimization results

reactor inlet temperature, °C	reactor outlet temperature, °C	iC5/C5P ratio	2,2-DMB/C6P ratio
111	86.3	74.1	31.0
117	91.6	75.7	34.0
105.6	95.4	75.6	33.2
115	95.6	76.1	34.4
113.4	100.4	76.7	34.3

The results show that the highest iC5/C5P (76.7%) ratio was reached at the reactor outlet temperature of 100.4 °C. The corresponding reactor inlet temperature was 113.4 °C. The highest 2,2-DMB/C6P (34.4%) ratio was reached at the reactor outlet temperature of 95.6 °C. The corresponding reactor inlet temperature was 115 °C. The lowest iC5/C5P and 2,2-DMB/C6P ratios were found at the reactor outlet temperature of 86.3 °C. The corresponding reactor inlet temperature was 111 °C. Operating below the maximum product ratio is operating in a rate-limited region. In this region, increasing the reactor outlet temperatures will increase the isomerization reactions and product ratios.[2] It was found that the highest 2,2-DMB/C6P ratio was reached at the reactor outlet temperature of 95.6 °C, which corresponded to the reactor inlet temperature of 115 °C. The iC5/C5P product ratios during the optimization were all below liquid equilibrium, most likely due to low reactor inlet temperatures and a possible slight loss of iC5. The optimum inlet start-of-run temperature for the lag reactor was set on 120 °C.[4]

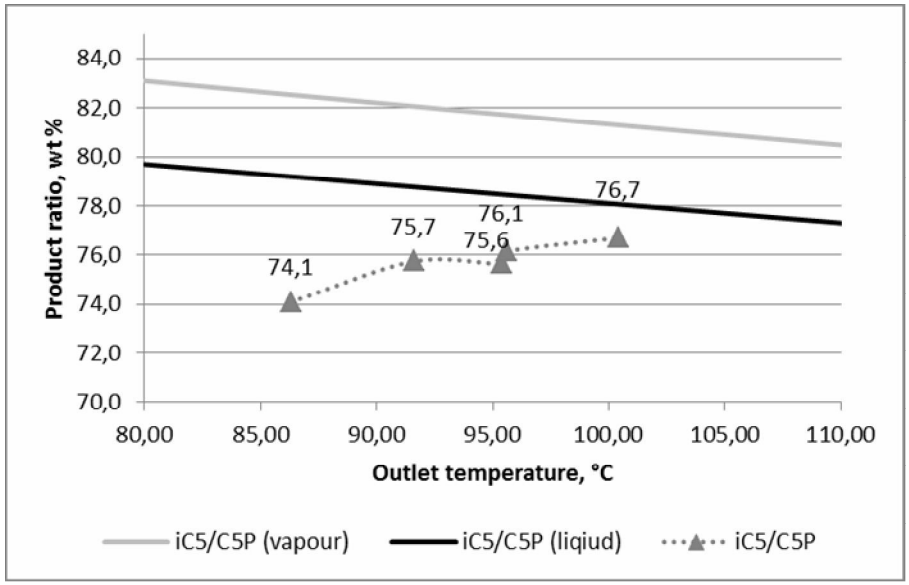

Figure 6: iC5/C5P product ratio in the lag reactor during optimization (LHSV = 1.33 h^{-1}; X = 4.3)

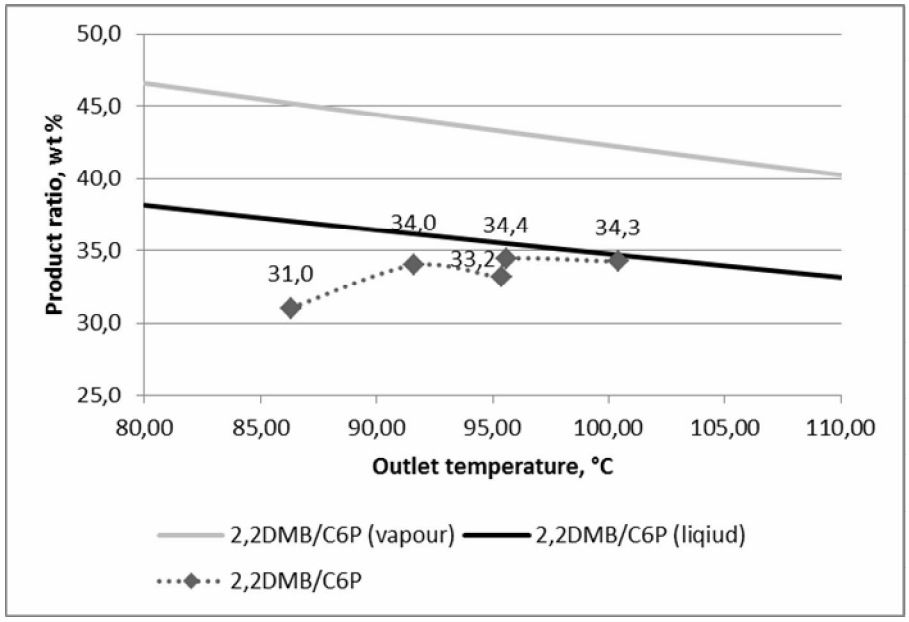

Figure 7: 2,2-DMB/C6P product ratio in the lag reactor during optimization (LHSV = 1.33 h^{-1}; X = 4.3)

If a maximum product octane is set as an economic goal, it is necessary to set the lead reactor outlet temperature to that point which provided maximum iC5/C5P product ratio and the lag reactor outlet temperature to that point which provided the maximum 2,2-DMB/C6P product ratio. For maximum octane-barrels, it is necessary to set the lead and lag reactor outlet temperatures to those points which provided the maximum iC5/C5P product ratios.[2]

4. Conclusion

The lead reactor temperature optimization was performed successfully. It was found that the highest product iso-ratios were reached at the reactor inlet temperature of 118.7 °C and the optimum inlet start-of-run temperature was set on 117 °C.

The temperature optimization was done under slight unstable feed conditions (LHSV, X factor) for the lag reactor due to time constraints. The results show that, at even this low reactor temperature during optimization, an increase in iC5/C5P ratio of 1.3 number was observed from lead to lag reactor. The lag reactor inlet temperature most likely has room for octane improvement with further rising lag reactor inlet temperature. The inlet start-of-run temperature for the lag reactor should be around 120 °C.

As the optimization was performed at throughput close to the unit design capacity, an optimization of reactor temperature optimization at low throughput could be performed. As the optimization was performed at throughput close to design capacity, in order to maintain optimal operation of the unit at lower throughput it is necessary to perform low throughput reactor temperature optimization.

The unit can be maintained close to its optimum by interpolation of the optimum reactor outlet temperatures between the extremes.

In addition, in order to verify if the reactors operate close to optimum without excessive hydrocracking it is necessary to monitor the reactor temperature trends, LHSV, X factor, iso-ratios, PIN/yield ratio.

Optimization of reactor temperatures should be performed periodically to identify optimal operating conditions and to reach desired product specifications.

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