Hydrogenation of pyrolysis gasoline in pilot trickle-bed reactor with periodic modulated feed rate

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Abstract

Comparison of both periodic and steady state hydrogenation of pyrolysis gasoline dissolved in toluene in pilot scale trickle bed reactor is reported. Enhancement of reaction rate under periodic operation mode is followed by higher mean catalyst bed temperature and broader pressure drop fluctuation with respect to steady state ones.

Keywords: pyrolysis gasoline, trickle-bed reactor, hydrogenation, feed rate modulation

1. Introduction

Hydrogenation of pyrolysis gasoline is widely applied in industry to prevent gum-formation and catalyst deactivation caused by dienes oligomerization (Nijhuis at al., 2003, Enache at al., 2005). Advantages of trickle bed reactor, which is usually adopted for this hydrogenation, consist in continuous operation, simple construction, etc. are accompanied by drawbacks like bad external heat exchange, liquid maldistribution and mass transfer limitation, namely concerning transfer of hydrogen to catalyst pellets (Dudukovic at al., 2002). Promising solution of these disadvantages can be periodic liquid feed rate modulation to create forced pulsing flow pattern in catalyst bed. Typical benefits are periodically renewal of wetted catalyst surface, more intensive interaction between gas and liquid phases in catalyst bed, higher mean reaction temperature and better of heat transfert during liquid rich part of feeding period, which result in higher reactor throughput, increased productivity and also operation safety (Silveston and Hanika, 2004, Banchero at al., 2004, Tukač at al., 2003).
The goal of this work was to compare hydrogenation rate of pyrolysis gasoline under both steady-state continuous feed and periodic modulated liquid feed rate carried out in pilot scale trickle–bed reactor.

2. Experimental

Trickle-bed reactor of 100 mm I.D. and 2000 mm height was equipped by automatic controlling and data acquisition system. Due to thick thermal insulation of the reactor, its behaviour was close to adiabatic regime. Catalyst bed depth 1000 mm of pelleted 0.1 % palladium on alumina catalyst (Degussa Noblyst 1505, mean diameter 3 mm) was applied for selective diene/olefinic bonds hydrogenation. Adiabatic reaction temperature rise for pyrolysis gasoline was controlled by solvent dilution to cca 10 %wt. dienes solution in toluene. Temperature and pressure axial profiles in catalyst bed were scanned with distance of 100 mm by thermocouples and pressure sensors (see Fig. 1). An excess of hydrogen to stoichiometric reaction demand at level 100 % was maintained in all experiments (Tukač et al., 2007).

Fig. 1. Photo of insulated pilot trickle bed reactor with set of thermocouples.
Typical composition of feed 24 % solution of pyrolysis gasoline in toluene is presented in Fig. 2. Label endo-dihydorcyclopentadiene instead of 2,3,3a,4,7,7a-hexahydro-1H-4,7-methano-indene is used.

Fig. 2. Proportional composition of representative unsaturated hydrocarbons in toluene solution of pyrolysis gasoline.

Most important reactive olefines are styrene including its derivatives (methylstyrenes), dicyclopentadiene and indene. These components represent more than one half of hydrocarbons mentioned.

3. Results and Discussion

During pilot plant tests a parametric sensitivity of the reactor behaviour to inlet temperature, pressure, and also to parameters of periodic liquid feed rate modulation mode like period length, its split as well as ratio of peak to base liquid feed rate has been investigated. Hydrogenation reactions in question exhibit important adiabatic temperature rise, which results in nonisothermal axial temperature profile. In case of periodic liquid feed rate modulation a higher mean temperature (Fig. 3) in the bed was found in comparison with steady state mode of operation using constant feed rate.
Periodic modulation of feed rate influences both pressure drop and temperature due to changing of dynamic liquid holdup (Giakoumakis et al., 2005). In contradiction to steady state operation, periodic modulation of this control parameter changes local value of catalyst bed heat capacity followed by temperature fluctuation. Extreme fluctuation of pressure drop at modulated liquid feed is caused by periodic flooding of void space in catalytic bed.

Sensitivity of axial temperature profile to parameters of periodic liquid feed modulation, like period length and split of period is demonstrated in Figs 4 and 5, respectively. Both figures represent time on stream records of temperature scanned by thermocouple located in catalyst bed.

Increase of temperature along catalyst bed is caused by accumulation of released reaction heat. Prolongation of length of period led to shortening of contact time due to prolongation of period part of poor liquid flow, and consequently to lower reaction rate and heat production. In the case of presented experiment, period prolongation causes steadily decrease of temperature. Steady state profiles at start and at the end of the record show somewhat lower magnitude of temperature in comparison with periodic ones.
Fig. 4. Catalytic bed axial temperatures vs. time on stream at steady state and periodic conditions. Mean feed rate 0.125 m$^3$ h$^{-1}$, different period 40, 60, 80 and 100 s, split 0.25

Influence of split of period is presented in Fig. 5. At the chosen conditions the system is much more sensitive and temperatures exhibit maximal values at minimal value of period split.
Influence of periodic feed rate modulation on conversion of sum of mode olefinic double bonds in reaction mixture is shown in Fig. 6. Experiment with two steady state continuous regimes preceding and followed of modulated feed operation was carried out with the best available split of period 0.15. A disadvantage of this split is necessity to pump in short time (only 15 % of period time) great amount of liquid to reach constant mean value. Due to low inlet temperature chosen (48 °C), a difference in conversion between steady state and periodic operation is small but clearly distinguishable.
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Fig. 6. Conversion of reactive (nonaromatic) olefinic double bond at steady state and periodic conditions. Mean feed rate $0.125 \text{ m}^3\text{ h}^{-1}$, period 60 s, split 0.15, inlet temperature 48 °C.

Selectivity of hydrogenation of individual compounds is evaluated like portion of its reaction rate of overall hydrogenation rate. Comparison of selectivity both for steady state and periodic operation is given in Fig. 7. At periodic modulated feed condition all monitored compounds exhibits higher relative reaction rate. Due to the high concentration of styrene and dicyclopentadiene in the reaction mixture, their hydrogenation is dominant is the reaction system.
Fig. 7. Selectivity of compound hydrogenation in form of partial hydrogenation rate to overall rate of hydrogenation at continuous and periodic modulated regimes.

Fig. 8. Influence of split on enhancement factor of individual components of pyrolysis gasoline. (Mean liquid flowrate 0.125 m³ h⁻¹, period 60 s, inlet temperature 69 °C).
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Ratio of periodic to steady state reaction rate named enhancement factor seems to be the best criterion of efficiency of periodic liquid feed modulation. In Fig. 8, an influence of parameter of modulation - split of period on enhancement factor of individual components of pyrolysis gasoline is presented. The shorter period split, the higher enhancement of hydrogenation of individual components. Only exception represents dicyclopentadiene with maximum enhancement at split 0.25.

It was stated, that mean reaction rate over whole catalyst bed (which represents reactor productivity) is higher at convenient modulation by 7% (cyclopentadiene – isoprene) to 20% for indene (see Tab. I) in comparison with the value typical for steady state mode of constant feed rate.

Tab. I: Enhancement factors of pyrolysis gasoline components.
Mean liquid flowrate 0.125 m$^3$ h$^{-1}$, period 60 s, split 0.25, inlet temperature 60 °C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Enhancement factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>styrene</td>
<td>1.072</td>
</tr>
<tr>
<td>allylenzene</td>
<td>1.130</td>
</tr>
<tr>
<td>3-methylstyrene</td>
<td>1.137</td>
</tr>
<tr>
<td>2- methylstyrene</td>
<td>1.155</td>
</tr>
<tr>
<td>4- methylstyrene</td>
<td>1.169</td>
</tr>
<tr>
<td>cyclopentadiene + isoprene</td>
<td>1.069</td>
</tr>
<tr>
<td>endo-dicyclopentadiene</td>
<td>1.090</td>
</tr>
<tr>
<td>indene</td>
<td>1.199</td>
</tr>
<tr>
<td>endo-dihydromercaptadiene</td>
<td>1.084</td>
</tr>
</tbody>
</table>

4. Conclusion

Hydrogenation of olefines and dienes in pyrolysis gasoline on palladium catalyst carries out selective with respect to preservation of aromatic ring of components. The most important compounds due to concentration and ability of polymerization are styrenes and dicyclopentadiene. To control adiabatic temperature rise of hydrogenation, the dilution of raw pyrolysis gasoline is necessary. The liquid feed modulation causes liquid and gas holdup fluctuation and catalyst bed periodic flooding, which result also in pressure drop and local temperature fluctuation. Sensitivity of reaction conversion and temperature to parameters of feed modulation in the tested range was evaluated. Increased period length led to mean temperature and conversion decrease. Period split value of 0.25 or shorter seems to be convenient for best enhancement of hydrogenation. Reaction rate enhancement by periodic modulation is more visible for minority components like indene.

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5. References


