

## LIQUID PYROLYSIS PRODUCTS PROCESSING TECHNOLOGY IMPROVEMENT

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*Existing technologies of pygas processing are considered. Styrene extraction from BTX cut by means of extractive distillation process is suggested for JSC "Salavatnefteorgsintez". Main benefits of this modernization are described.*

*Keywords: extractive distillation, solvent, separating, styrene, BTX, aromatics, pyrolysis, pygas, model, HYSYS, Wilson*

The profitability increasing policy is constantly carried out at JSC "Salavatnefteorgsintez". For manufacturing divisions it means new state-of-the-art units construction and modernization of existing plants that improves their products' competitiveness.

One of prospective investment projects at the company is the pyrolysis unit EP-700. Thus total ethylene capacity will be increased from 300 kta that current EP-300 unit supplies up to 1 Mta.

Increasing of capacity will make reasonable the implementation of many technologies that increase total efficiency of pyrolysis plants and reduce the cost of the main product. One of the most prospective areas of such technologies is liquid pyrolysis products processing technology improvement.

Liquid are called all the pyrolysis products that are in liquid aggregative state at normal conditions. Usually they are fractionated on two cuts – pyrolysis gasoline (C<sub>5</sub> - C<sub>8</sub>, pygas) and heavy fuel oil (C<sub>9</sub> and higher). Pygas consist mostly of aromatic (benzene and its homologes), olefinic and naphthenic hydrocarbons; fuel oil – of high-molecular compounds of aromatic, naphthenic and naphtheno-aromatic series.

Heavy oil is generally used as a fuel (moderate calorific value, low sulfur content), in certain cases it can be used as a feed for production of coke, carbon black, petroleum polymer gums, pitches etc.

Pygas is the most valuable by-product of pyrolysis process, so the optimization of its processing is of particular importance. Let's consider two main ways of pyrolysis gasoline processing: fuel and petrochemical.

a) Use of pygas as a component of commercial gasoline. High aromatics content determines high octane number. Hydrotreating of the fraction is required to eliminate unsaturated and sulfur-containing compounds for the production of chemically stable gasoline. In addition, benzene content in gasoline will be sternly restricted by prospective specifications. So its recovery is required when the pygas is used as a blending fuel.

b) Production of individual aromatics (benzene, toluene, xylenes). Existing technologies differ one from another by the product range, capital and operating expenditures.

Economic efficiency of each alternative is determined by the market prices of products, chemical composition and the quantity of processing pygas. The second way is most probably optimal in the case of complex refinery and petrochemical plant, because it allows to produce feed for own petrochemical units. Whereas for the production of high-octane blending fuels alkylation, FCC and isomerization units are preferable.

Flow chart of the liquid pyrolysis products processing at JSC “Salavatnefteorgsintez” is presented on figure 1.

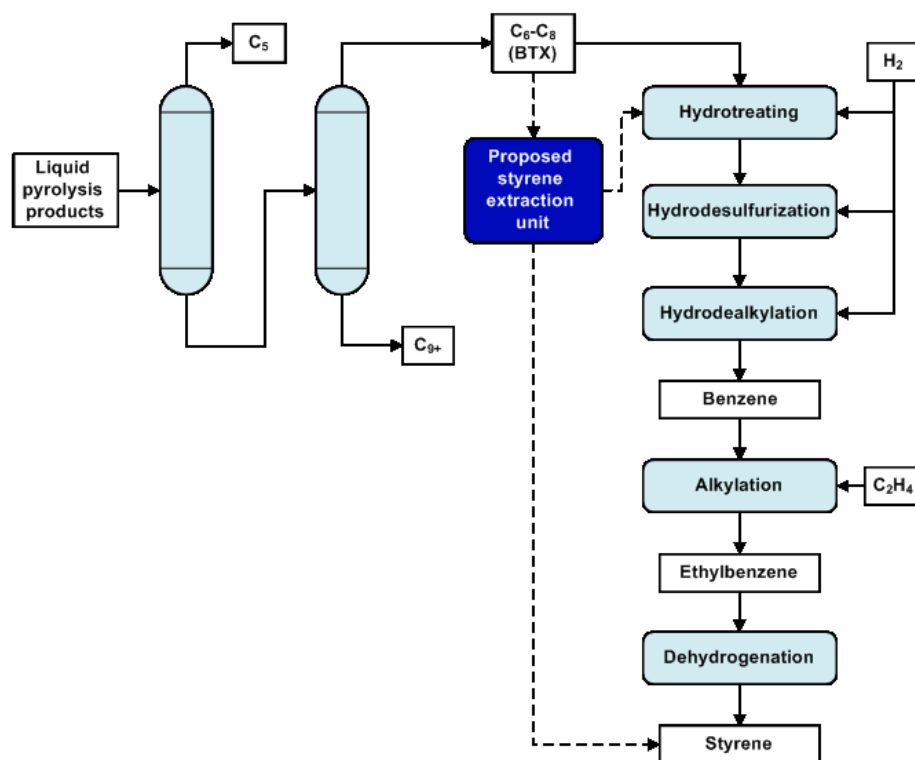


Figure 1 – Flow chart of the liquid pyrolysis products processing at JSC “Salavatnefteorgsintez”

Firstly, penthane-amylene cut  $C_5$  is recovered from the flow. Remained  $C_{6+}$  cut is fractionated on benzene-toluene-xylene (BTX) and  $C_{9+}$  cut. BTX is subjected to hydrotreating, hydrodesulfurization and hydrodealkylation in a cascade of reactors with obtaining of benzene. Then benzene is alkylated by ethylene up to ethylbenzene. Ethylbenzene is dehydrogenated with obtaining of styrene.

Present scheme can be upgraded by the extraction of styrene from BTX cut. Such modernization gives following advantages:

1) Workload and coking in hydrotreating reactors is decreasing which leads to increasing of palladium catalyst run length.

2) Hydrogen rich gas consumption on hydrotreating and hydrodesulfurization of BTX cut is decreasing.

3) Ethylene consumption per ton of total styrene production is decreasing.

4) In the conventional scheme ethylbenzene content is increased in BTX after hydrotreating in consequence of styrene hydrogenation. BTX with low ethylbenzene content in suggested scheme is similar to BTX cut of the reforming process. It allows to process them together for the production of xylenes.

5) According to existing scheme the heaviest part of  $C_8$  cut is joined with  $C_{9+}$  cut in column C-2 (figure 1) to decrease coke formation in hydrotreating reactors. Preliminary extraction of styrene allows to lower the cut point and enlarge raw materials base of benzene production process.

In our study we evaluate practicability of styrene extraction process implementation in JSC “Salavatnefteorgsintez”.

GOST 10003-90 establishes following specifications on commercial styrene:

- styrene consumption: above 99,8 % mass;
- phenylacetylene: below 0,01 % mass.

Presence of phenylacetylene is utterly undesirable in the styrene intended for polymerization as it affects polystyrene quality. There is a deal of phenylacetylene in liquid pyrolysis products though, and its separation from styrene is practically impossible. Therefore it is necessary to lower the content of this impurity by means of selective hydrogenation for high-quality styrene production.

Recovery of styrene-containing C<sub>8</sub> cut from pyrolysis gasoline is essential to improve process selectivity and reduce solvent consumption. Boiling temperatures of its components are given in table 1 [2, 3].

Table 1

Boiling points of C<sub>8</sub> cut components

| Component       | Boiling point, °C |
|-----------------|-------------------|
| Ethylbenzene    | 136,2             |
| p-xylene        | 138,4             |
| m-xylene        | 139,1             |
| o-xylene        | 144,4             |
| Styrene         | 145,2             |
| Phenylacetylene | 145,3             |

As it is shown in table 1, boiling points of styrene and some other components are very close. Therefore styrene extraction from this cut by means of conventional distillation is practically impossible.

In contrast to other aromatic components of the cut, styrene has double bond in the side chain. This structural difference allows to choose selective solvent and change thereby relative volatilities of the compounds to separate. Then the extractive distillation can be used for styrene recovery.

The main difficulty when developing such a process is choosing of solvent. It should meet following demands:

- 1) to have high selectivity;
- 2) to have sufficiently high boiling point (low volatility) for easier separation with the substance to be extracted (styrene).
- 3) to be low-toxic and have low corrosion activity;
- 4) to be presented in adequate amount at a reasonable price in the region where its usage is planned.

Properly selected solvent better solves the substance to be extracted (styrene) and in a less degree – all the other components of cut. Selective action of the solvent is based on a difference in interaction powers of its molecules with styrene molecules and with the other constituents of mixture. This difference can be caused by the polarity of substances, hydrogen bonds and other factors.

Thus when the molecules of styrene are surrounded by solvent molecules, minimal energy needed to move them into the gas phase increases. Thereby the volatility of styrene is decreased forcibly. So relative volatility of  $C_8$  cut components and styrene is increased, because the styrene is the heaviest of them. Therefore it is necessary to maintain high concentration of solvent in liquid phase of mixture [5].

N-methylpyrrolidon, N,N-dimethylacetamide, sulfolane, methylcarbitol, ethylcellosolve, propylenecarbonate etc. are examined as a solvent for the styrene extraction process in different researches. It is often recommended to use the mixture of organic solvent with water. Besides reducing consumption of the main solvent it improves separation efficiency.

Flow diagram of styrene recovery by extractive distillation process is given on figure 2.

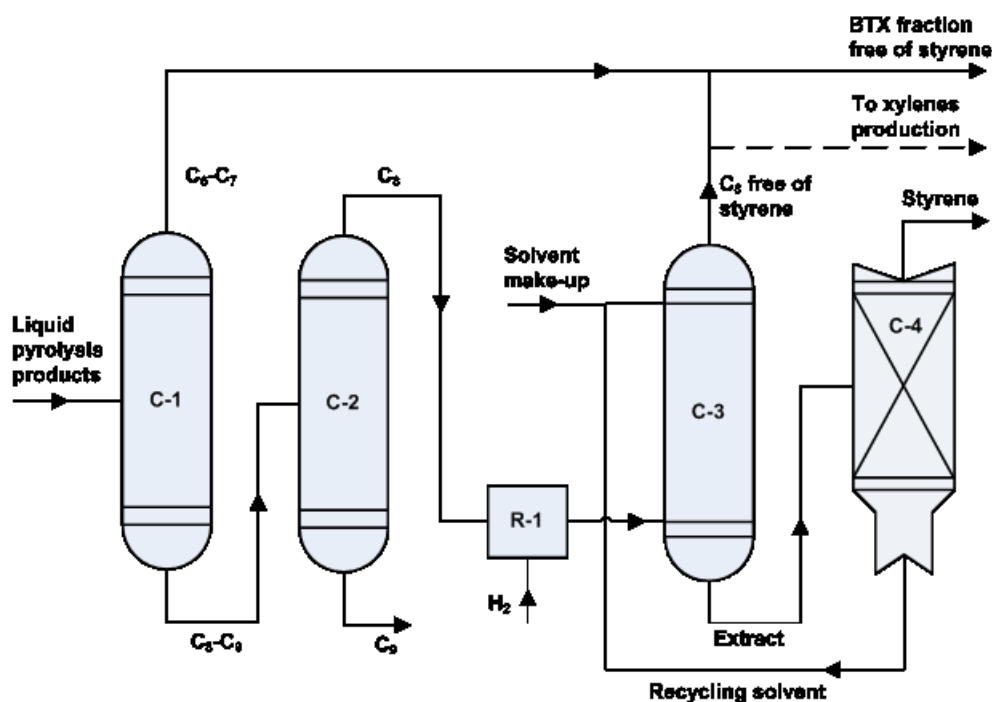


Figure 2 – Styrene extraction process:

C-1, C-2 – fractionating columns; R-1 – phenylacetylene hydrogenation reactor;  
C-3 – extractive column; C-4 – vacuum column.

Benzene-toluene cut ( $C_6$ - $C_7$ ) which is the feed for benzene production, is distilled from the top of C-1 column.  $C_{8+}$  cut from the bottom of C-1 goes to C-2 column.  $C_8$  fraction is cut from the top of C-2 and feeds R-2 reactor where phenylacetylene is selectively hydrogenated up to styrene.

Solvent is added to  $C_8$  cut in extractive column C-3. It is fed on tray 5-7 from the top to maintain high concentration along the whole height of column. Solvent is fed in liquid phase. It has high boiling point, so 5-7 trays is enough to minimize its content in distillate. The mixture to be separated is fed to bottom part of column. Overhead product of extractive column is  $C_8$  fraction free of styrene. It is merged with  $C_6$ - $C_7$  and sent to benzene production (or can be processed separately for xylenes production). Bottom product (extract) consists mostly of solvent and styrene.

Then extract is separated on styrene and solvent in C-4 column. Separation is carried out under vacuum to avoid polymerization of styrene. Styrene from the top of C-4 goes to further processing, and solvent is recycled to C-3 column.

We have built mathematical model of suggested process in HYSYS program. It simulates  $C_8$  cut separation from liquid pyrolysis products and further styrene recovery from this cut by means of extractive distillation. Wilson activity model was chosen to calculate vapor-liquid equilibrium (VLE) in columns. Model adequacy was experimentally proved on a laboratory column.

According to the literary data [4], implementation of described technology will be efficient if styrene production reaches 20 kta and higher. With present capacity of EP-300 unit in JSC "Salavatnefteorgsintez" styrene output could be about 7 kta. But in consideration of that company plans to build EP-700 pyrolysis unit, quantity of liquid pyrolysis products will raise more than three times. Then styrene extraction from pygas will have sufficient affordability.

## CONCLUSIONS

Recovery of styrene from pyrolysis gasoline requires relatively low investments (3 additional columns, no reactors or other costly equipment), but gives several significant advantages to the technology of it processing. We consider this process to be promising in near-term outlook. Researches should be directed on selection of optimal extractive solvent to get better industrial performance.

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