Synthesis of Para-Xylene via Toluene Methylation

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Background & Description:

his project investigates the simulation of a selective para-xylene (p-xylene) production process from toluene methylation using the proprietary chemical process simulator Aspen HYSYS. p-Xylene is a high-demand industrial compound used in the synthesis of terephthalic acid, essential for the production of polyethylene terephthalate (PET), widely found in textile fibers and plastic bottles.

Due to the very close boiling points of the xylene isomers, the conventional separation of p-xylene from m- and o-xylene through crystallization or adsorption is both energy-intensive and costly. An alternative process involves the direct methylation of toluene using methanol over a shape-selective H-ZSM-5 catalyst to selectively form p-xylene and water. The advantage of this approach lies in its potential to produce p-xylene directly, minimizing costly downstream separations.

The primary reaction governing the synthesis is:

Toluene + Methanol → p-Xylene + Water

The production process is simulated in Aspen HYSYS and comprises the following steps:

1. **Reaction**: Toluene and methanol are pumped from storage conditions (25°C, 1 bar) to 3 bar, and preheated to 400°C. The vapor-phase reactants are fed into a Plug Flow Reactor (PFR) modeled with an Arrhenius-type kinetic law. The reactor has a volume of 60 m^3 and a length of 1 meter. The kinetic expression is, with k in $kmol/m^3 \cdot h \cdot atm$ and TTT in Kelvin.

$$r = k \cdot C_{Toluene} \cdot C_{Methanol}, k = 244800 \cdot \exp(-RT46100)$$

2. **Cooling and Condensation:** The vaporous reactor effluent is cooled down to 50°C using a cooler to condense heavy components.
3. **Distillation:** A shortcut distillation column separates the light overhead fraction containing methanol and water, from the bottom fraction composed mainly of p-xylene and trace water.
4. **Decantation**: The bottom product is further cooled and sent to a 3-phase separator, which acts as a decanter. Due to the immiscibility between water and p-xylene, two liquid phases form, enabling gravity-based separation.

The simulation used the NRTL thermodynamic property package to ensure accurate modeling of polar (water, methanol) and non-polar (aromatics) interactions, especially for the decanter behavior.

Despite the use of a Shortcut Column, the simulation successfully separated methanol-water overhead and a p-xylene-rich bottom stream. The 3-phase separator efficiently doesn't split the bottom into an aqueous phase and an organic phase composed primarily of high-purity p-xylene.

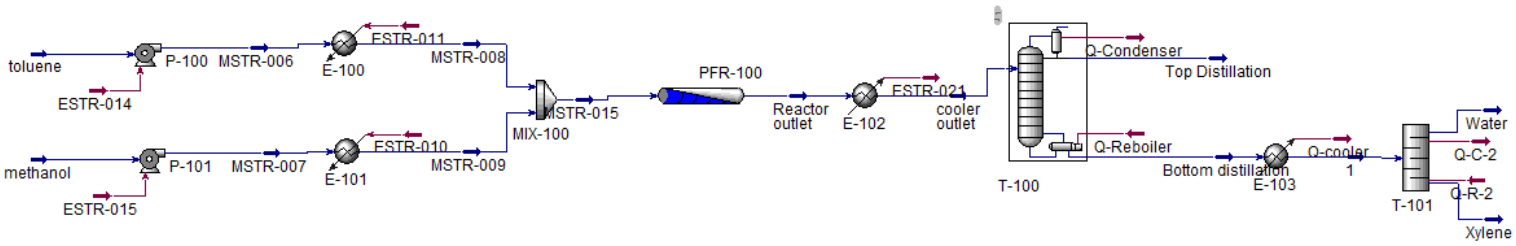
Initial issues with the lack of phase split were resolved by:

- Lowering the temperature of the bottom product to below 50°C.
- Ensuring the use of the NRTL model for accurate phase behavior.
- Providing sufficient feed composition contrast between water and p-xylene.

The process achieved a p-xylene molar purity of over 99% in the organic phase, and toluene conversion exceeded 99.9%.

Thermodynamic package: NRTL was selected as the primary property method due to its suitability for mixed polar/non-polar systems and its ability to predict liquid-liquid phase separation (LLE) essential for the decanter simulation. Its reliability in handling mixtures containing water, methanol, and aromatic hydrocarbons makes it preferable over cubic equations of state like Peng-Robinson.

Flowsheet



Results:

Master Property Tableau								
Object	**Toluene**	**Methanol**	**MSTR-015**	**Reactor outlet**	**Top Distillation**	**Bottom distillation**	**Water**	**Xylene**
T (°C)	**25.00**	**25.00**	**400.0**	**575.6**	**68.83**	**118.0**	**100.0**	**138.5**
P (bar)	**1.013**	**1.013**	**3.013**	**2.948**	**1.013**	**1.013**	**1.013**	**1.013**
Molar Flow (kgmole/h)	**188.8**	**393.7**	**582.5**	**582.5**	**295.5**	**287.0**	**98.57**	**188.4**
Mole Fract (H2O)	**0**	**0**	**0**	**0.3235**	**0.3041**	**0.3435**	***0.9999***	**0.0001**
Mole Fract (Methanol)	**0**	**1**	**0.6758**	**0.3523**	**0.6945**	**0.0000**	**0**	**0**
Mole Fract (p-xylene)	**0**	**0**	**0**	**0.3235**	**0**	**0.6565**	**0.0001**	***0.9999***
Mole Fract (toluene)	**1**	**0**	**0.3242**	**0.007**	**0.0014**	**0.0000**	**0**	**0**

Nb : Insignificant quantities (<0) of components in the product streams can be considered negligible, effectively approximating them to zero without impacting the overall process results or conclusions (see flowsheet).

References: Ashraf, M. T., Chebbi, R., & Darwish, N. A. (2013). Process of p-Xylene Production by Highly Selective Methylation of Toluene. Industrial & Engineering Chemistry Research, 52(44), 13730–13737. https://doi.org/10.1021/ie401156x