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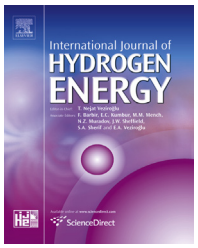

# Hydrogen recovery from the purge stream of a cyclohexane production process using a mass exchange heuristic

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ABSTRACT

In this paper, we propose a novel hydrogen recovery structure in a cyclohexane production process, arrived at by following a mass exchange heuristic developed in previous works [1,2].

In the cyclohexane production process considered, we explore the effect of process design variables and find the optimal design for a mass exchange between the purge stream and the feed of benzene to the process. We compare our results with a conventional process design lacking hydrogen recovery from the purge, and with a process design which implements a conventional membrane recovery system at the optimum setup of the decision variables. The process with recovery through mass exchange here proposed obtained a respectable 7.12% reduction of hydrogen consumption, resulting in an increase of the plant Net Annual Income of a 4.24% respect to the conventional process design without recovery. These figures are similar to the ones that result from implementing a process design with a conventional membrane recovery system. These results highlight the importance of considering a mass exchange between the process feed and purge stream as an alternative design of the recovery system.



## Introduction

The design of a new process following the hierarchical procedure by Douglas [3,4] advances in the design generating more detailed versions of the process with an increasing number of process blocks interconnected by process streams. The design procedure is guided by heuristics, which recommend among the options available at each stage of the design, e.g. definition of the input–output structure of the flow sheet, definition of the recycle and separations structure, etc.

The technique for the synthesis of Mass Exchange Networks (MENs) [5–7] dictates mass exchanging between process streams in a counter-current arrangement, as much as possible. This technique needs as input, the list of streams to be integrated, their flows and inlet-outlet concentrations. Therefore, the mass integration methodology is naturally being applied to existing processes, or in the final stage of a new process design once all streams have been generated.

In previous works [1,2,8,9], we proposed and described in detail the use of the concept of Mass Exchange Network as a

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mass exchange heuristic at two levels of Douglas [3,4] hierarchical process design procedure. We considered applying the mass exchange heuristic to a process that involves a reaction between two or more gas-phase reactants, performed at medium or high pressure, which react to form a product and eventually byproducts. Usually, some of the reactant is fed in excess to either expedite or complete the reaction, so that this reactant is found in abundance in the reactor outlet stream, together with the product and some byproduct or any inert component fed together with the other reactants. The reactant added in excess, after separation from the reactor product, is recycled to the reactor inlet, and a purge is extracted from the recycle to prevent accumulation of inert components and/or byproducts.

We proposed to use the mass exchange heuristic at the higher level of the hierarchical design procedure of Douglas [3,4] (after defining the reaction, when deciding the structure of the recycle and separation system). At this level, we can exchange mass between the stream exiting the reactor (rich in a reactant) and a reactor inlet stream (without or with a poor concentration in the same reactant). The reactant in the stream leaving the reactor is at a high partial pressure, while in the stream that feeds the reactor, this reactant has a null or low partial pressure. Thus, we have a considerable gradient of partial pressure to transfer this reactant, even if the stream entering the reactor was already pressurized. The driving force for mass exchange in gas permeation membranes is always the difference in partial pressure of the component of interest across the membrane, but this driving force is provided by the concentration gradient rather than by the trans membrane total pressure. At this level, the heuristic can be stated as "after the reaction is defined, tray integrating streams entering and exiting the reactor (or after a flash separation in our case) to recover the valuable reactant".

The purge stream is also rich in the reactant added in excess, so we can apply the mass exchange heuristic also at the last design refinement step of the hierarchical design procedure, leading to exchange reactant between the purge stream rich in it, and a reactor inlet stream lean in the same component. At this level, the heuristic can be stated as "once all process streams have been generated, tray to integrate streams entering to the reactor and purge streams exiting the process, to recover the valuable reactant".

In the process design literature there exist several modified hierarchical procedures to extend the original by Douglas [3,4] to new applications, for example the paper by Douglas [10] to waste minimization, Rossiter and Douglas [11,12] to handle solids operations, Steffens et al. [13] to biotechnology separations, or by Konda et al. [14] to include process control. It is out our goal to do the same to include countercurrent mass exchange into the design procedure. However we still lack enough casuistic to support a general new hierarchical procedure.

We successfully applied the mass exchange heuristics to a process for the synthesis of Biodiesel [8], the synthesis of Benzene from Toluene (HDA Process) [1,2], a Cyclohexane production process [15] (in this case at the higher hierarchy level), and an Ammonia synthesis loop [9], resorting to a novel counter-current mass exchanger equipment (a gas permeation membrane module) previously presented [1].

This paper focuses on analyzing the new recycle alternatives generated in a cyclohexane synthesis process, when applying the mass exchange heuristic at the end of the hierarchical design procedure, which leads to integrating streams entering and exiting the process [7]. To model, simulate and optimize the process, as well as to perform various analysis, we resorted to the following software: Aspen Plus V8.2, Aspen Custom Modeler V7.2, Aspen Energy Analyzer V7.2 and Aspen Process Economic Analyzer V7.2.

Following, there is a brief description of the Cyclohexane synthesis process Hydrar. Afterwards we assess different recovery systems: the conventional recovery system design using a gas permeation membrane along with diverse recovery system alternatives arrived at by using the mass exchange heuristic. Next, we analyze the economic impact of adopting the proposed new design and compared it with both conventional process designs, with and without recovery system. Finally, the last section draws the conclusions of this work.

## Cyclohexane synthesis process

### *Overview*

To illustrate the application of the mass exchange heuristic at the end of the hierarchical design procedure, we will use the Hydrar Process (Universal Oil Products, U.O.P. now a Honeywell company). In this process [16] the hydrogenation of benzene to cyclohexane is performed in a series of adiabatic reactors under controlled conditions allowing the reaction to occur at a temperature, as low as possible. The reactants are drawn out from each reaction zone, cooled through steam generators, combined with more benzene and sent into the following reaction zone, where this sequence is repeated. There can be many reactors in series, although too many complicate the controllability of the process. Therefore, four reactors is usually the choice. In this process, the gaseous mixtures of benzene, cyclohexane and hydrogen (with their impurities) at a temperature between 163.33 °C and 204.44 °C and a pressure between 6.9 bar and 35 bar are fed to the adiabatic reaction zones were they contact the catalyst. The gases are removed from the reactors at temperatures between 260.00 °C and 315.55 °C, cooled down to temperatures between 163.33 °C and 204.44 °C and sent to the next reaction zone. The cyclohexane and hydrogen pass in series through all the reaction zones, while the benzene stream passes in parallel, with a fraction being derived to each reaction zone to be hydrogenated. It may be split in equal parts or in proportions such that the exit temperature of each reaction zone does not exceed a target value, usually not higher than 300 °C. In each of the reaction zones, the final conversion of benzene is sought to be complete to prevent further separation of benzene from cyclohexane downstream of the reaction. The reaction exit stream contains cyclohexane, hydrogen and their impurities or inert gases (normally methane and nitrogen from make-up hydrogen). Most of the hydrogen and impurities are separated from the cyclohexane using a partial condenser, followed by a flash that separates the light gases, which are recycled after purging some of this stream, to prevent the accumulation of impurities in the process.