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Original Research

Process Design of Benzene Nitration

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Abstract*—Aspen HYSYS was used to investigate several aspects of process design for benzene nitration. In this study, the frequency factor (k_o) and the activation energy (E_a) for benzene nitration were given from the literature. Calculations of chemical and physical properties were performed automatically on Hysys using the NRTL and UNIQUAC Thermodynamic models. Some aspects of process design were studied, namely: (1) the effect of temperature on the conversion of reactions, (2) the effect of the ratio of sulphuric acid to nitric acid on the synthesis of nitrobenzen in the reactor, and (3) the effect of reactor arrangements (parallel and series) on reaction conversion. The results showed that the peak of conversion that could be achieved on a single reactor was 96.9% at a ratio of sulfuric acid: nitric acid = 3.5 and a temperature of 50ºC. However, based on this study, it is suggested that the most favorable conditions for nitation of benzene in an isothermal reactor are 50°C and a sulfuric acid:nitric acid ratio of about 2.5 to 3.*

Keywords: *hysys, nitration, nitrobenzene, reaction, simulation*

Abstrak—Aspen HYSYS digunakan untuk menginvestigasi beberapa aspek perancangan proses pada nitrasi benzen. Energi aktivasi (Ea) dan faktor frekwensi (ko) untuk reaksi ini diperoleh dari literature. Perhitungan sifat-sifat fisis dan kimia dilakukan secara otomatis pada Hysys dengan menggunakan model Termodinamik NRTL dan UNIQUAC. Beberapa aspek perancangan proses dipelajari dengan simulasi, yaitu: pengaruh suhu pada konversi reaksi, pengaruh rasio asam sulfat terhadap asam nitrat pada sintesa nitrobenzen dalam CSTR (reaktor berpengaduk kontinyu), dan pengaruh susunan reaktor baik seri maupun parallel terhadap konversi reaksi. Hasil penelitian menunjukkan bahwa konversi tertinggi yang dapat dicapai pada CSTR tunggal adalah 96,9 % pada rasio asam sulfat: asam nitrat = 3,5 dan suhu 50ºC. Namun demikian, berdasarkan penelitian ini, disarankan bahwa kondisi yang paling disukai untuk nitasi benzen dalam CSTR isotermal adalah 50ºC dan rasio asam sulfat:asam nitrat sekitar 2,5 sampai 3.

Kata kunci: *hysys, nitrasi, nitrobenzen, reaksi, simulasi*

INTRODUCTION

Chemical process industries are related to the application of the principles of the physical sciences together with the principles of economics and human relation to fields that pertain directly to process and equipment in which matter is treated to affect changes in state, energy content or composition (Austin 1984).

Nitration is a unit proces for the introducing nitro group into organic chemical compounds. The benzene nitration is an example of electrophilic aromatic substitution (Hoggett 2009; Nitration and Aromatic Reactivity - J. G. Hoggett, R. B. Moodie, J. R. Penton, K. Schofield - Google Books. [no date]). NO_2^+ or the nitronium ion is the electrophiles and individually react with aromatic benzene to produce nitrobenzene. Protonation of nitric acid by sulphuric acid is considered the source of nitronium ion, which brings on the loss of water molecule and formation of nitronium ion.

Nitrobenzene is an aromatic nitro compound and has recently received great attention because of its acute toxicity, refractoriness, mutagenicity, teratogenicity and resistance to degradation. Nitrobenzene has been widely used as an intermediate in the manufacture of agricultural chemicals, explosives, plastics, lubricating oils, dyes, and paint additives. As a raw material and important product of the chemical industry, nitrobenzene has been commercially by pharmaceutical industry to produce analgesic drugs such as paracetamol, phenacetin, and acetanilide. In addition, a large amount of 95 % nitrobenzene is used in the production of aniline, which is an indispensable chemical precursor, is toxic, and is easily absorbed hypodermically, even at very low concentration, endangering life (Rafique et al. 2023).

Nitrobenzene has been produced commercially since the early nineteenth century by nitration / nitration of benzene (Kobe and Mills 2002). The production of nitrobenzene is one of the most dangerous processes conducted in the chemical industry because of the exothermicity of the reaction (ΔH = −117 kJ/mol). It was first synthesized from Benzene and fuming nitric acid in 1834. Human exposure may occur both by inhalation and by skin absorption during its production and use. Nitrobenzene has been detected in surface and groundwater (Nitrobenzene (IARC Summary & Evaluation, Volume 65, 1996)). Since that time the nitration of benzene has been the subject of many studies, and some researchers have determined useful data for industrial implementations (Biggs and White 1956).

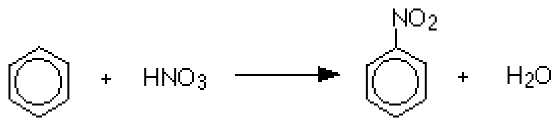
A mixture of concentrated nitric acid and sulfuric acid is called mixed acid. In the synthesis of mixed acid, sulfuric acid acts as a catalyst as well as a water absorber.

The reaction of benzene nitration is usually carried out at $50°C$ to ensure for only one nitro group. The mixture is held at $50°C$ for about half an hour. The nitrobenzene product is oily and yellow liquid.

The reaction equation is as follows:

$$C_6H_6 + HNO_3 \Rightarrow C_6H_5NO_2 + H_2O \quad (1)$$

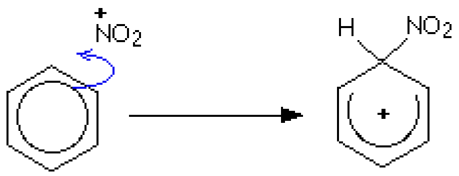
or:



(2)

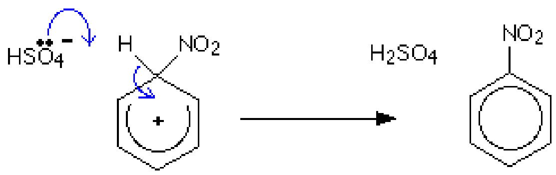
The electrophilic substitution mechanism can be divided into two stages:

Stage 1:



(3)

Stage 2:



(4)

Chemical process industry research into the benzene nitration process has reached many precious improvements including better energy management of modern nitration plants and various clean nitration approaches focusing on the use of sulphuric acid (Gong et al. 2010). The catalyst (sulphuric acid) is expensive to recovered and creates environmental issues that make benzene nitration one of the most dangerous chemical process industries. Hence, many studies have focused on the application of different catalyst material (Gong et al. 2010; Ganjala et al. 2014; Koskin et al. 2014; Kulal et al. 2016).

A pilot plant for the continuous nitration was made by Quadros (Quadros et al. 2005). The following equations correlates k_0 and E_a with the weight fraction of sulphuric acid S :

$$k_0 = e^{\left[166.64S^2 - 254.36S + 113.79\right]} \quad (6)$$

$$E_a = (-283.88S + 263.37) \times 1000 \quad (5)$$

With the availability of process simulators such as Aspen Hysys, process design can be done easier and faster, because mathematical modeling for the process is not an easy job. This study aims to simulate reaction of benzene at various temperatures, various ratios of sulphuric acid to nitric acid, and the reactors arrangement. Its scope is mainly for nitration reactor. The conversion percentage will be displayed above the temperature for a particular loading task in the reactor.

METHOD

Materials

All materials involved in the reaction are available in the component list of HYSYS.

Instrumentation

Computer with Aspen HYSYS software will be used to simulate the process

Procedure

This research is conducted as follows (Figure 1).

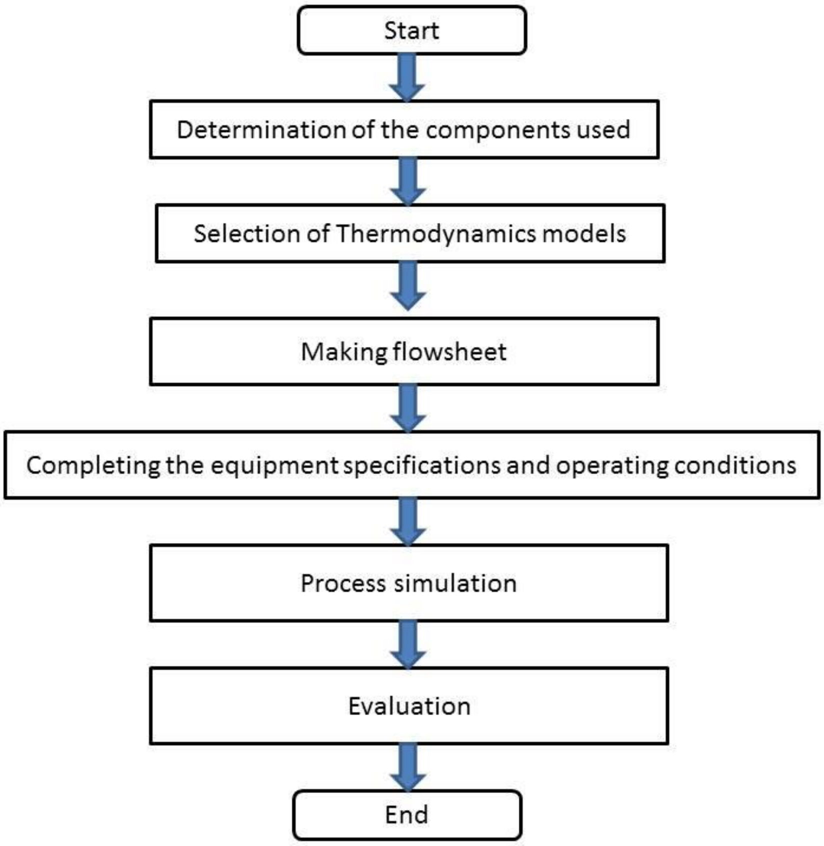


Figure 1. Research methodology framework.

In this study isothermal reactor (Continuous Stirred Tank Reactor) was used. Table 1 shows the reactor dimension and operating conditions of the process being studied; and Figure 2 shows the process fow chart for the nitrobenzene production system.

Table 1

Reactor Dimension and Operating Condition

Operating conditions	Values	
Mass flow benzene	1000	kg/h
Concentration of benzene	89.99	%
Mass flow of nitric acid	1173	kg/h
Concentration of nitric acid	65	%
Mass flow of sulphuric acid	2561	kg/h
Concentration of sulphuric acid	89	%
Reactor diameter	1.221	m
Reactor height	1.832	m
Pressure	101.3	kPa
Liquid volume in the reactor	80	%

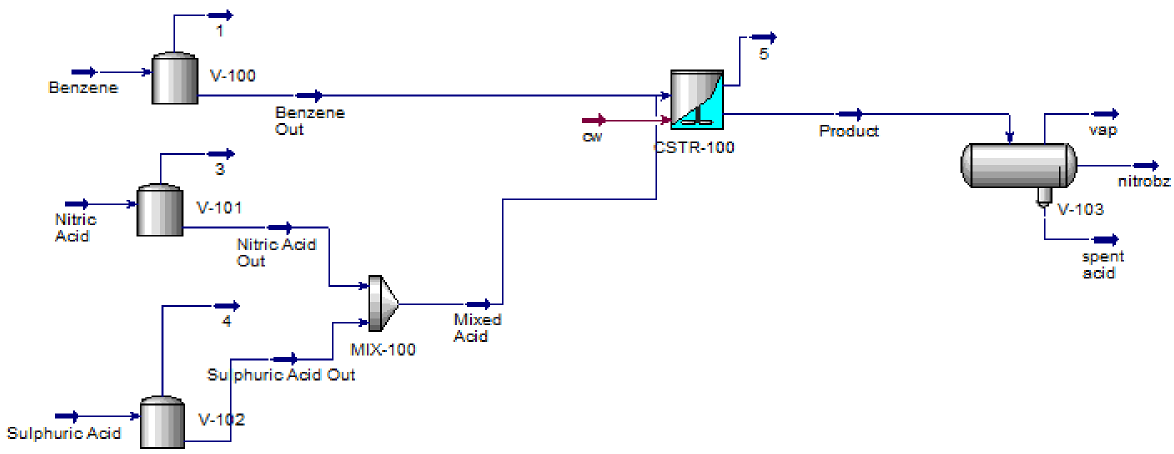


Figure 2. Flow chart for benzene nitration.

The process would be simulated for the following conditions:

- The operating temperatures were varied between $20°C$ - $50°C$ with an interval of 1^oC.
- Comparison of the ratio of sulphuric acid to nitric acid which was varied between 2.5 to 3.5 with an interval of 0.1.
- The main equipment setup: parallel and series.

RESULTS AND DISCUSSION

One thing that needs to be considered in HYSYS simulation is the selection of fluid packages used to predict the physical properties involved in the process. NRTL and UNIQUAC are examples of thermodynamic models suitable for liquid phase process. The two thermodynamic models give similar results, hence NRTL was chosen as the fluid package for this study. All physical properties were computed automatically at HYSYS.

The Effect of Temperatures

The temperature used in this study is limited to the range of $20°C$ - $50°C$ on a basis of $1000\,kg$ of benzene per hour. Reactor operating temperature should not exceed $50°C$ to avoid the formation of dinitrobenzene by-products (Clark 2000). The acid mixture consists of 60% sulphuric acid and 20% nitric acid and the remainder of the water. The residence time in the in the reactor was 30 minutes.

Figure 3 below shows that the conversion will increase with increasing temperatures. These results have been presented previously (Agustriyanto et al. 2017a). This is in accordance with research conducted by Quadros (Quadros et al. 2005) stated that the increase in temperature is proportional to the increase in the conversion of benzene nitration. The effect of temperature on the reaction kinetic thus indirectly affecting the conversion.

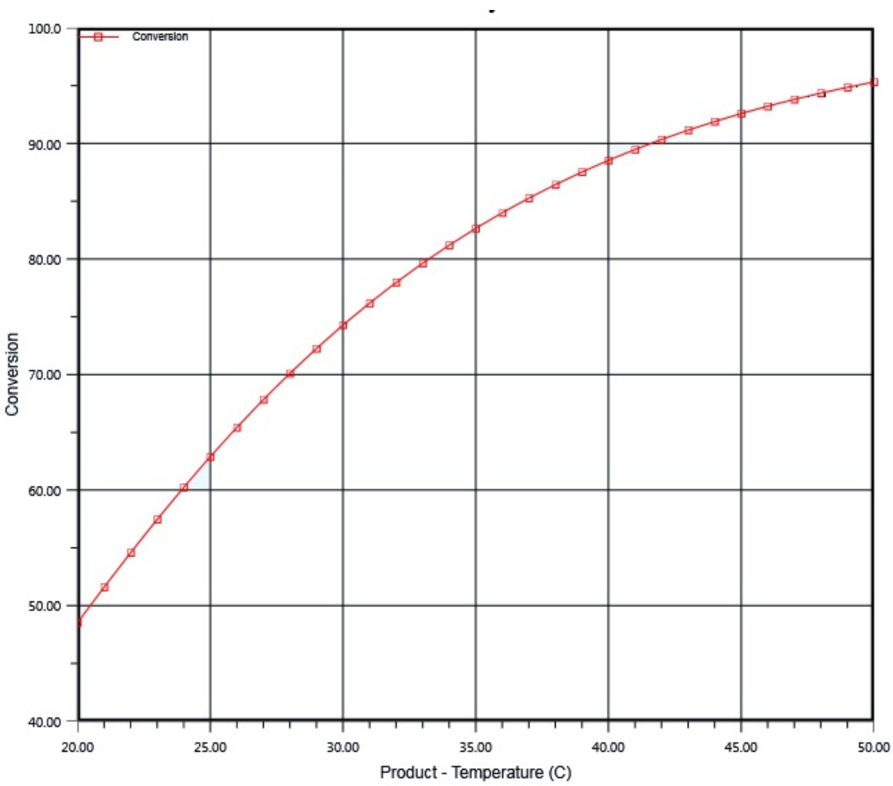


Figure 3. Plot of conversion vs operating temperature.

Effect of Mixed Acid Ratio (Sulphuric Acid : Nitric Acid)

The reaction of benzene nitration is also affected by the acid concentration in the catalyst mixture used.

Figure 4 shows that the conversion will increase with increasing temperature and increasing the ratio of sulphuric acid to nitric acid (Agustriyanto et al. 2017b). At low temperatures, the ratio of sulphuric acid to nitric acid greatly affects the conversion reactions. Nevertheless, at high temperatures the effect of this ratio is not significant. This behavior can be seen more clearly in Figure 5, where the ratio vs. conversion curve at higher temperatures is almost straight line.

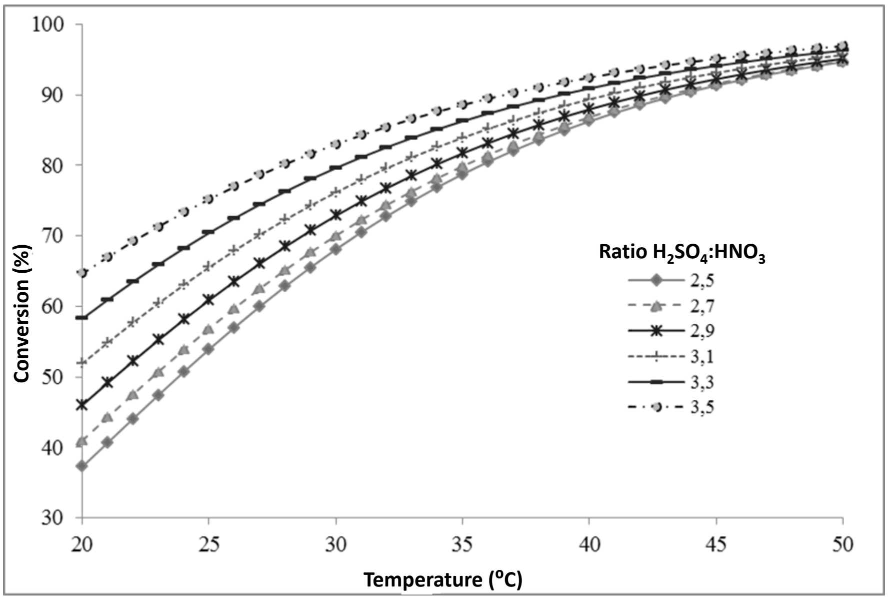


*Figure 4***.** Plot of conversion vs temperature for different ratios of H_2SO_4: HNO_3

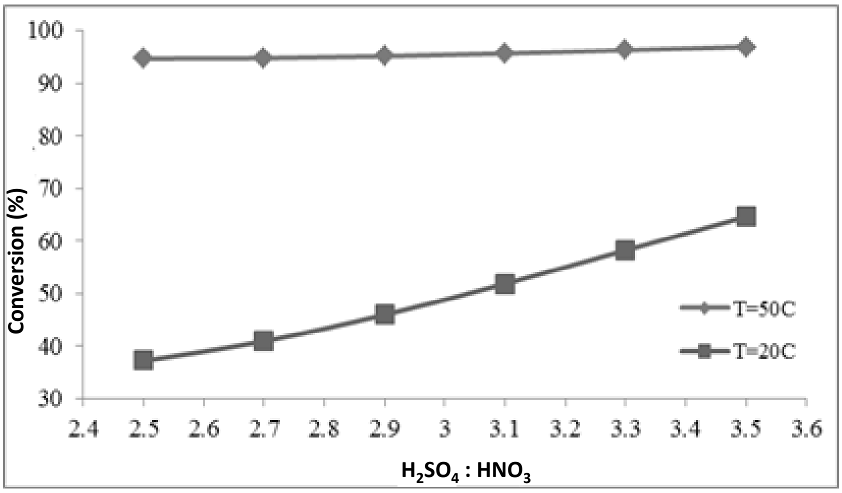


Figure 5. Plot of conversion vs ratio of H_2SO_4: HNO_3 at temperatures of $50°C$ and $20°C$

Reactor Setup

Variation of the two reactors (parallel and series) for different volumes were also carried out. The results shown in Table 2 suggest the use of a series arrangement because it provides a more conversion than a parallel.

Table 2

Overall Conversion for Parallel and Series Reactor Arrangement

	V_1 $[m^3]$	V_2 $[m^3]$	**Overall Conversion**	
			Parallel	**Series**
1	0.10	0.10	81.7733	87.6041
2	0.10	0.20	84.5400	90.7054
3	0.10	0.30	85.8142	92.3265
4	0.10	0.40	86.5857	93.3698
5	0.10	0.50	87.1162	94.1145
6	0.10	0.60	87.5092	94.6807
7	0.10	0.70	87.8151	95.1298
8	0.10	0.80	88.0615	95.4971
9	0.10	0.90	88.2655	95.8046
10	0.10	1.00	88.4377	96.0668
11	0.20	0.10	84.5400	90.3664
12	0.20	0.20	87,3067	92,7148
13	0.20	0.30	88.5809	93.9742
14	0.20	0.40	89.3524	94.7946
15	0.20	0.50	89.8829	95.3839
16	0.20	0.60	90.2759	95.8336
17	0.20	0.70	90.5817	96.1911
18	0.20	0.80	90.8282	96.4839
19	0.20	0.90	91.0322	96.7293
20	0.20	1.00	91.2044	96.9385

CONNCLUSION

Study of process design aspect for benzene nitration has been carried out. It has been discovered that the reaction conversion in a continuous isothermal reactor increases with increasing temperatures. The increase in the ratio of sulphuric acid to nitric acid is proportional to the increase in conversion.

The peak conversion that can be achieved with a single reactor is 96.9% at a temperature of $50°C$ and a ratio of sulphuric acid : nitric acid = 3.5. Therefore, the most favorable conditions for the benzene nitration in an isothermal reactor are an operating temperature of $50°C$ and a low sulphuric acid : nitric acid ratio.

The use of two reactors in series can synthesize nitrobenzene with better conversion with a smaller size compared to a single reactor or 2 reactors with parallel arrangement.

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