Determination of optimal feed profile in semi-batch reactor: DFT and experimental studies on a Case Study of parallel and serial reactions take place

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Abstract

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Abstract

Semi-batch reactor systems can be used at different areas due to its advantages of the feed manipulation. Common practices are temperature control of the exothermic reactions or selectivity adjustment of the production process include serial and parallel reactions. Bisphenol A (BPA) is theoretically synthesized with 2 moles of phenol and 1 mol of acetone. During the reaction, a stoichiometric ratio or high acetone concentration causes the formation of by-products. This situation has been confirmed by density functional theory (DFT) calculations. In these calculations, the B3LYP method and the 6-311++G(d, p) basis set were used. DFT calculations show that by-products can be formed in the synthesis of bisphenol a. The common method used to solve the by-product problem is to work with high molar phenol/acetone ratios. But this brings additional operating and investment costs. In this study, semi-batch reaction experiments were performed which stoichiometric acetone was fed in reactor with various pulsed modes in the presence of homogenous and heterogenous catalysts. Time versus conversion and selectivity data were collected at various catalyst concentrations. All runs were compared with the results of batch and semi-batch runs

performed in over molar ratio of phenol/acetone. As a result, it has been shown that high conversion and selectivity can be achieved by providing energy efficiency with pulsed mode semi batch reactor.

KEYWORDS

DFT, BPA, Pulsed feed, Semi batch, Selectivity

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1 | Introduction

Bisphenol-A (BPA) is a very important material for production of polycarbonates, epoxy resins and many other polymers. BPA is synthesized with condensation reaction of phenol and acetone in acidic media (Figure 1).

Figure 1. BPA synthesis reaction with phenol-acetone condensation.

Sulfuric acid and hydrochloric acid are used as catalyst for the traditional production method. Besides, ion-exchange resins extensively are used as catalyst in industry. BPA must have minimum 95% purity for the epoxy resin production and 99% and upper purity for the polycarbonate synthesis (Wang et al., 2014; Yadav et al., 1997). Depending on the reaction conditions and catalyst types, many by-products occurs in the process of BPA production. In the literature there are various studies to increase yield and selectivity. These studies generally are catalyst works conducted for the purpose of eliminating disadvantages of the mineral acid usage. The common property of these studies is feeding phenol to acetone molar ratio greater than stoichiometric ratio (from 3:1 to 10:1). The reason is to eliminate the by-products occurring self-condensation of acetone and the others (Yadav et al., 1997). However, operational cost, which includes pumping, heating, distillation, is increased with high phenol feeding in this way. As mentioned above high concentration of acetone in reaction media increases by-products due to self-condensation of acetone and side reactions. The most common by-products formed at the end of the reaction are summarized in Figure 2.

Figure 2. Formation of by-products with the high amount of acetone.

As known essentially in semi-batch systems, it is possible to manipulate the concentration of reactants in re-action media at the desired levels to obtain high yield and selectivity, also wild exothermic reactions can be controlled with these systems. There are different semi-batch studies based on yield and selectivity in literature. Because of its industrial importance, works conducted on BPA synthesis are generally encountered in the patent literature (Nowiska & Kaleta, 2000; Jeřábek et al., 2002; Kawase et al., 1998; Chen et al., 2008; Hou et al., 2006; Singh, 1992; Das et al. 2004; Wang et al., 2013; Jia et al., 2004; Park et al., 2006; Laufer et al., 2002; Ouk et al., 2003; Al-Megren et al., 2013; Callanan et al., 2012; Tan et al., 2015; Santacesaria et al., 2011; Maestri & Rota, 2013). Nowiska and Kaleta synthesized a new catalyst with encapsulation of 12-tungstophos-phoric acid (HPW), ammonium and cesium salts on the MCM-41 for liquid phase BPA production. They compared yield and selectivity with synthesized catalyzer and zeolite (H-Y, H-DY). They carried out experiments at certain temperatures, reaction times and phenol-acetone molar ratios. They found highest selectivity (%60) with CsHPW/MCM catalyzer, feeding of 3:1 phenol-acetone molar ratio, at 160° in 6 hours (Nowiska & Kaleta, 2000). Jerabek and his colleagues used ion-exchange resins as catalyzer to synthesize BPA. They chose sulfonated divinyl benzene and Amberlyst as catalyzer. They investigated activity and the swelling properties of these catalyzers. They used CSTR microreactor to prevent the problems that come with catalyzer swelling in batch systems. They achieved the highest reaction rate with sulfonated divinyl benzene (%1 by weight), feeding ratio of phenol to acetone 8:1 at 70° (Jeřábek et al., 2002). Lastly, Maestri and Rota, compared semi-batch reactors and semi-batch recycle reactors which designed for preventing the further reaction of main products with by-products hence selectivity loss. They developed boundary diagrams which can be used to identify selectivity and reactor productivity just using operating conditions and with these diagrams no need to solve mathematical model of the system (Maestri & Rota, 2013). However, in all of these studies, bisphenol a synthesis could not be synthesized in an appropriate yield or amount. It is not considered appropriate for them to be produced on an industrial scale. In addition, many by-products were obtained. Therefore, this study aims to eliminate the disadvantages (energy costs) of the pre-said situation. For this purpose, semi-batch reactor type was selected and experiments were conducted at stoichiometric ratio in various feeding modes. Acetone was fed as pulsed flow in a semi-batch operation. Feeding and waiting time were changed systematically and best result was explored for high yield and selectivity. Besides, batch and semi batch studies results, which were conducted in stoichiometric and over stoichiometric ratios were compared. The effect of mercaptoethanol as a catalyst enhancer, the amount of catalyst on product yield and selectivity was also investigated. As a result, the optimal feeding mode was determined to achieve high efficiency and selectivity with stoichiometric ratio aimed the minimum operating

cost.

2 | Materials and Methods

2.1 | Materials

Phenol, Amberlyst-15 and mercaptoethanol from Sigma Aldrich, acetone and 37% HCl from Carla Erba were used in these all experiments. Shimadzu GC-FID/2014 was used for the analysis. The method of analysis was found in literature (Neagu, 1998). The analysis method is as follows: The first 2 minutes column temperature is 50 °C. The column temperature increases to 250 °C with a ramp that lasts for 4 minutes with an increase of 50 °C per minute. Then the column temperature is held at 250 °C for 6 minutes. The detector temperature is 320 °C. Thus, the total analysis time for a sample is 12 minutes.

2.2 | Experimental Setup and Procedure

BPA production reaction which results from the reaction of 2 moles of phenol with 1 mol of acetone. In practice, this reaction cannot be carried out efficiently using stoichiometric ratios. This is due to the formation of isomers and derivatives of BPA and the self-condensation of acetone in series and parallel reactions (Mcketta & Cunningham, 1977). In order to prevent this, practically high phenol:acetone ratios are preferred. This ensures that the acetone concentration is kept low in the reaction medium. But this will actually lead to an increase in energy costs as well. Based on this challenge, the operating conditions of the semi-batch reactor using stoichiometric phenol/acetone ratio were investigated.

In semi-batch experiments, 0.4 moles of acetone were fed into the reactor during the 6 hours reaction time that previously added 0.8 moles of phenol, at various flow modes (pulsed mode). In order to keep the concentration of acetone in the media to a low level, it was fed to the reaction medium in a semi-batch condition. The semi-batch feeding was performed in various modes (45-15, 50-10, 60-30, 75-15, 90-30, 120-60, 180-180, 360-0 and batch 1-359).

In these modes the first term indicates the feeding time as minute and the seconds referee the waiting time (stopping the feeding). In the experiments firstly, 37% HCl was used as catalyst and 5%, 15% and 25% of the total reactants by mole were added to the medium. The reactants were stirred at 800 rpm and reacted at 60 °C and the reaction continued for 6 hours. Samples were taken at 4, 5 and 6th hours and analyzed. In addition, solid Amberlyst ion-exchange resin was also used as catalyst. Catalyst was added 10%(w/w) of the reactants to the reaction medium. In batch experiments, phenol and acetone were added to the reactor at a various molar ratios and the experiments were carried out under the above conditions. The results were compared with the experiments performed at 2:1, 3.5:1 and 5:1 etc. molar ratios of phenol-acetone. The semi-batch experiment system is shown in Figure 3.

Figure 3 Semi-batch system for BPA synthesis by phenol-acetone condensation.

2.3 | DFT Calculations

The bisphenol a was obtained from the reaction of phenol with acetone, but, many by-products can be formed in addition to the target product. In this section, the reaction mechanism is theoretically examined and the energies of the bisphenol a and by-product, TS and intermediate are calculated. Thus, the formation possibilities of products and by-products were investigated theoretically. All molecules were optimized using Density functional theory (DFT)/ B3LYP method (Becke, 1993) and 6-311++G(d,p) basis set. In addition, harmonic frequencies of the structures were calculated at the same method and basis sets to find a local minimum (all positive force constants) or transition states (one imaginary force constant only). All calculations were performed with Gaussian 09 program package (Frisch et al. 2009).

3 | Results and Discussion

3.1 | DFT Calculations

The most likely by-products that may occur in the bisphenol a synthesis have been determined from the literature. These byproducts are methiclyl oxide, chroman I, chromanII and triphenol compounds. By examining each product and by-product mechanism, possible product, ancestor product and transition states that may occur are modeled. All defined molecules were optimized in DFT / 6-311 ++ G (d, p) method and base set. It has been proven that they are optimized at minimum energy by performing frequency calculations. Optimized structures and relative energies of the calculated molecules are shown in Figure 4, and the relative energy values are listed in Table 1.

Figure 4. Relative energies between reactans, phenol + acetone and product as bisphenol a, by-product as mesityl oxide, chroman I, chroman II, triphenol I, and their TS, intermediate.

Table 1. Relative energy of the reaction paths for synthesis of bisphenol a and by-product, TS and intermediate.

Molecule	Relative energy (kJ/mol)
1	0.00
2-TS	184.98
3	36.33
4-TS	103.59
5	26.20
6-TS	156.85
7-Bisphenol A	-53.25
6-TSt	233.12
7-Tripyhenol	56.70
2-TSm	204.33
3m	105.72
4-TSm	193.02
5-mesityloxiide	-8.55
6-TScI	193.42
7cI	54.48
8-TScI	110.43
9cI	29.35
10TScI	128.65
11-ChromenI	-65.13
6-TScII	189.52
7cII	48.31
8-TScII	105.73
9cII	34.48
10-TScII	134.51
11-ChromenII	-65.32

When Figure 4 and Table 1 are examined, as a result of the reaction of phenol and acetone, the relative reaction energy of bisphenol a was calculated as -53.25 kJ / mol. It has been found that among possible intermediates, chroman molecules can be obtained with higher energy than bisphenol a. The relative energy of the chroman I and chroman II molecules was calculated as -65.13 and 65.32 kJ / mol, respectively. Other expected products indicate that the mesityl oxide compound may form as a by-product, although the formation of mesityl oxide and triphenol compounds is low. The step determining the reaction rate for all products and by-products is the first step. The relative energy of these steps was calculated as 184.98-233.12 kJ / mol. Although the reaction with the lowest transition state energy is bisphenol a, especially chroman compounds I and II are likely to form as byproducts. Small amounts of mesityl oxide and triphenol by-products are also expected to form. According to these results, synthesis and synthesis cost of a bisphenol molecule, which is widely used commercially, is very important. In this context, it is very important to get rid of by-products that are unavoidable during the reaction and to ensure that energy costs are minimized. For this reason, experimental studies are designed to reduce by-products and reduce raw material and energy costs in the following sections.

3.2 | HCl Catalyst Results

The selectivity and conversion values obtained from semi-batch experiments in various feed modes using 5% HCl catalyst are given in Table 2. In general, conversion and selectivity are lower at 5% acid concentration.

All selectivity values are below 91% from 0.81 and the average value is around 0.87 ± 0.028 . It is understood that the average conversion is around $26\% \pm 0.035\%$. The selectivity tends to remain almost constant and conversions increasing are being observed over time.

An increase of approximately 15% in conversion between each hour, regardless of acid concentration is noticeable (Table 2). When the acid concentration increases from 5% to 15%, conversions increase by more than 60%. When the acid concentration increases from 15% to 25%, it is encountered that the increase in conversion is about 20%. Selectivity values between the modes do not show very obvious relationships because the acetone concentration in the medium varies with the feeding modes, and many series and parallel reactions in the reaction medium depend on this acetone concentration. When it is looked at the data, which 25% acid concentration is used, it is seen that the selectivity is 91% for continues feeding mode (360-0) and 88% for batch mode (1-359). Interestingly, the selectivity values for '60-30' feeding mode (similar to the other acid conc.) are lower than the other feeding modes, while the others showed almost similar selectivity.

Again, generally the highest conversion and selectivity are observed in cases where the acid concentrations are 25%, as can be seen from Table 2. Although, 54% conversion and 95% selectivity are peak values, the selectivity shows an average value of 0.92 ± 0.02 . In the case of using 15% acid concentration, the values of selectivity (94%) belong to the 5th and 6th hours of '45-15' feeding mode are close to the values when using 25% acid concentration. Selectivity value is 89% at 15% acid concentration in 180-180 feeding mode. Also '90-30' feeding mode shows similar performance. The '45 -15' mode is therefore used as the basis for conducting further trials. As can be seen from the tables, in many trials, the impurities actually occur during the first 4th hour, after which they either fall or remain almost constant.

The higher selectivity values at the 15% acid concentration in the '45-15' feeding mode (the need for low acid usage) led to the progression through this mode as previously mentioned. Afterwards, studies were conducted in over ratios (3.5/1, 5/1) in '45-15' feeding mode. The effect of co-catalyst usage was also investigated in batch and semi-batch systems. The results are given in Table 2.

In the case where 25% HCl and the co-catalyst are used, 97% selectivity was attained at 6th hours. Although, the conversions in the 3.5/1 and 5/1 mole ratios are higher than stoichiometric ratio '45-15' feeding mode, the selectivity's are lower. In these experiments, no co-catalyst was used, and if used, it is estimated that it would provide a 20 percent increase in returns and improvements in selectivity would be observed. Again, in the case of batch stoichiometric run was carried out with co-catalyst, the conversion increased from 49% to 60% and the selectivity increased from 85% to 91%.

By-products form undesired colors as mentioned before. Lighter color obtained with semi-batch system. Parameters are same for both experiments except semi-batch was applied with 45-15 feeding mode.

Table 2. The results of experiments performed with HCl catalyst.

Feeding Mode (min-min)	Phenol/ Acetone	HCl %	4th hour
using 5% HCl as catalyst	using 5% HCl as catalyst	using 5% HCl as catalyst	Selectivity using 5% HCl as catalyst
45-15	2:1	5	0.85
50-10	2:1	5	0.89
60-30	2:1	5	0.86
75-15	2:1	5	0.81
90-30	2:1	5	0.89
360-0	2:1	5	0.88
180-180	2:1	5	0.89
120-60	2:1	5	0.87
1-359	2:1	5	0.81
using 15% HCl as catalyst	using 15% HCl as catalyst	using 15% HCl as catalyst	using 15% HCl as catalyst
1-359	2:1	15	0.88

Feeding Mode (min-min)	Phenol/ Acetone	HCl %	4th hour
45-15	2:1	15	0.92
50-10	2:1	15	0.82
60-30	2:1	15	0.89
75-15	2:1	15	0.93
90-30	2:1	15	0.90
120-60	2:1	15	0.93
180-180	2:1	15	0.88
360-0	2:1	15	0.91
using 25% HCl as catalyst	using 25% HCl as catalyst	using 25% HCl as catalyst	using 25% HCl as catalyst
1-359	2:1	25	0.92
45-15	2:1	25	0.92
50-10	2:1	25	0.91
60-30	2:1	25	0.89
75-15	2:1	25	0.93
90-30	2:1	25	0.94
120-60	2:1	25	0.93
180-180	2:1	25	0.95
360-0	2:1	25	0.89
use of phenol and co-catalyst	use of phenol and co-catalyst	use of phenol and co-catalyst	use of phenol and co-catalyst
45-15	5:1	25	0.92
45-15	3.5:1	25	0.95
45-15+co	2:1	25	0.97
1-359+co	2:1	25	0.82

3.3 | Amberlyst Catalyst Results

After the studies with HCl catalyst, studies were conducted with Amberlyst which is more environmentally friendly and simple to separate from the reaction medium. The results are given in Table 3. In the studies conducted with Amber-lyst catalyst, 2.3% conversion was achieved in the batch experiment, while this value remained at 1.4% in the ‘45-15’ feeding mode, also 50% increase in selectivity is observed. In the batch run with the co-catalyst, the conversion was increased to 3% and the selectivity increased to 94%. It is understood that the co-catalyst has a great effect on selectivity here. In the trial where the excess ratio was studied (5-1), the conversion reached 5% and the selectivity remained at 66%. Again, it is obvious in the case of using co-catalyst a positive contribution in conversion and selectivity is possible. As a result, it is understood that in the ‘45-15’ mode, with 15% HCl catalyst, high conversion and selectivity can be achieved without spending too much HCl. The Amberlyst catalyst, although environmentalist, is inadequate in conversion. The use of co-catalyst provides significant improvement in the system in all cases.

Table 3. The results of experiments performed with Amberlyst catalyst.

Phenol/ Acetone	4th hour	4th hour	5th hour	5th hour	6th hour	6th hour
	Selectivity	Yield	Selectivity	Yield	Selectivity	Yield
2-1 (batch)	0.50	0.012	0.50	0.018	0.43	0.023
2:1 (45-15)	0.75	0.01	0.53	0.013	0.64	0.014
5-1 (batch)	0.57	0.04	0.61	0.048	0.66	0.052
2:1 (batch)+co	0.88	0.024	0.9	0.028	0.94	0.03

3.4 | Chemcad Calculations

The Chemcad program was used to calculate the heat loads required for the distillation column and the energy required for pre-heating and reactor cooling. This simulation was conducted based on the conversion data obtained from the experiments. The results are given in Table 4. The data in the Table 4 were handled on the basis of 10 kg acetone. Acetone was pre-heated with stoichiometric or excess phenol and then fed into the reactor. The energy calculation was examined based on the conversion in the experimental results. Then the mixture obtained from the reactor was subjected to distillation and the heat loads required for the boiler and condenser were examined. Preliminary trials have shown that the change in the number of trays does not substantially change the amount of energy required for the condenser and the reboiler. This brings up the results of the following; the difference between the boiling points of phenol and BPA is too high, therefore effect of the number of trays to be low. It was observed that the amount of energy consumed in the condenser and reboiler increased with the increase in reflux rates while the number of trays was constant. However, the separation time was reduced but this did not decrease significantly. The amount and duration of energy required for the separation to be realized was determined by simulation. All experiments were carried out for a column with 5 trays and reflux rate of 0.25. A total of 95476 kJ of energy is required as a result of the batch experiment with a phenol-acetone feed at a molar ratio of 10:1, and 16671 kJ of energy is required in a 2:1 molar ratio. Increase in the amount of phenol appears to increase the amount of energy in the boiler about 6 times. Again, the energy requirement in the condenser is about 9 times higher. It is seen that 4 times more energy is needed for pre-heating and about 1.5 times more energy is required for reactor cooling.

Table 4. Energy requirements obtained by Chemcad simulation program.

Mole ratio	Feeding Mode	x (%)	Distillation Condenser (kJ)	Distillation Reboiler (kJ)	Reactor (kJ)	Heat Exchanger (pre heater) (kJ) .
10-1	1-359	100	-82384.1	95476	-15850	12736
5-1	45-15	72	-37742.9	47627.1	-11440.1	6863
3.5-1	45-15	69	-22145.6	30548.2	-10968.9	5091.8
2-1	45-15+co-cat.	60	-9346.56	16671.5	-9576.2	3334

4 | Conclusions

In the bisphenol a synthesis reaction, different by-products are obtained with many serial and parallel reactions. This result has also been demonstrated as a result of DFT studies, in this paper. Therefore, the solution proposal was investigated in the laboratory environment. Originated high concentration of acetone, high molar phenol/acetone ratios are being used in the industry to prevent serial and parallel reactions in the reaction medium. This imposes energy costs on the plant. Studies in this paper were carried out based on above challenge. In a semi-batch reactor working at stoichiometric ratios, acetone feed profile which will achieve high conversion and selectivity also the effect of catalyst type and concentration of HCl were investigated. It has been found that '45-15' feeding modes are the best among the various feed profiles. Also, the amount of HCl increased from 5% to 15% conversions increased by 60% and increasing HCl percent from 15% to 25% conversion increased around 20%. With the increase of the amount of HCl from 5% to 15%, the selectivity has increased from 87% to 91.5%. The highest conversion with the Amberlyst catalyst was obtained as 5.1 with 5/1 phenol-acetone ratio with a selectivity of 60%. Using Amberlyst in the presence of co-catalyst in the stoichiometric ratio, the selectivity increased from 64% to 94% and conversion from 1.4% to 3%. The use of co-catalyst has been shown to contribute positively to conversion and selectivity in all cases. The energy required for reboiler in the distillation column is 95476 in the case of 100% acetone conversion at molar ratio of 10/1 mol. In the case of 60% conversion at molar ratio of 2/1 and co-catalyst usage, the energy requirement is 16671. It is understood that the energy requirement is 6 times greater. While 60% conversion and %85 selectivity were obtained at molar ratio of 2/1. In the '45-15' feeding mode 60% conversion and 97% selectivity were achieved. At this manner effective result was obtained both energy

and selectivity aspects. As a result, pulsed feed semi-batch reactors are seen as usable in many similar processes in the energy, selectivity and efficiency axis.

Supplementary Information (SI)

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/.....>

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Compliance with ethical standards

Conflicts of interest

There are no conflicts to declare.

Author contribution

Bugra AKMAN: Software, Validation, Formal analysis, Investigation, Data Curation, Writing- Original Draft, Ömür ARAS: Conceptualization, Methodology, Software, Formal Analysis, Data Curation, Writing- Original Draft, Visualization, Supervision, Project Administration, Funding acquisition, Yunus KAYA: Formal Analysis, Resources, Data Curation, Funding acquisition

Code availability

MATLAB 2020A and CHEMCAD 7.1.4 which provided by Computer labs. of Bursa Technical University used in this study. Figures were created by Microsoft Paint, MATLAB 2020A and ChemBioDraw Ultra 12.0

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