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Research Article

Improving Net Energy of Cumene Hydroperoxide Production using Cumene Oxidation Process Through Removing Cooler on the Recycle System to Achieve Energy Efficiency and Reduce Production Cost

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Abstract

This study investigates a modification to the cumene hydroperoxide (CHP) production process by removing the cooler between the reactor and separator, aiming to improve energy efficiency. The simulation results show that the modified process requires 245,259,223.09 kJ/h, compared to 265,992,099.05 kJ/h for the basic process, representing a significant energy reduction of 20,732,875.95 kJ/h. The removal of the cooler also leads to lower capital and operating costs, with annual savings of $111,900 in operating costs and $103,580 in utilities. This modification enhances the overall energy efficiency and cost-effectiveness of the CHP production process while maintaining product selectivity and operational performance.

Keywords: Cumene Hydroperoxide; Energy Efficiency; Process Simulation; Aspen HYSYS; Cost Reduction

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1. Introduction

The production of cumene hydroperoxide (CHP) through the oxidation of cumene is a crucial process in the chemical industry, as CHP serves as a precursor in the synthesis of various chemicals, including phenol, propylene oxides, acetone, etc. [3]. CHP is used in many applications on previous search such as evaluates the systemic toxicity of CHP, its effects on free radical production, and antioxidant levels following dermal exposure in animal models. This research contributes to understanding the safety and handling of CHP in industrial applications [18]. Another paper discusses the use of CHP as an initiator for polymerization processes, particularly in the production of acrylonitrile–butadiene–styrene (ABS). It highlights the thermal hazards associated with CHP and its interactions with metal ions, which are crucial for ensuring safety in chemical manufacturing [19]. Additionally, a journal article also discuss the applications that focuses on simulating the production of cumene and its derivatives, including CHP. It discusses optimization techniques that enhance efficiency in industrial processes, providing insights into the practical applications of CHP in chemical manufacturing. These journals collectively provide valuable information on the applications and implications of cumene hydroperoxide across various industrial contexts [20]. Previous search

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also talk about study contributes to understanding how CHP can be utilized not only as an intermediate but also as a valuable feedstock in chemical manufacturing [21]. The demand for cumene hydroperoxide (CHP) as a raw material is increasing. CHP is used as an agent in the synthesis of propylene oxide, and it is also utilized as a synthesis agent in crosslinking agents for polymers [17]. In industry, this reaction can be carried out by reacting cumene with atmospheric oxygen at moderate temperature and pressure. Due to the possible occurrence of various side reactions (i.e. formation of dimethyl phenyl carbinol, acetophenone, formic acid, etc.), a small per-pass conversion of cumene is more favorable to avoid selectivity loss [5]. However, it often faces challenges related to high operational costs and capital investment, particularly concerning the use of inefficient cooling and separation equipment. Numerous studies have been conducted on the development of innovative catalysts [2], kinetic modeling [3], reactor design [1]., and safety assessments [6] related to the oxidation of cumene. The balance between enhancing conversion, selectivity, and minimizing production costs has garnered significant research interest [5]. Nevertheless, comprehensive models for the cumene oxidation process have been scarcely proposed in existing literature, which hampers further advancements in process design, optimization, and control. Additionally, considerable efforts have been made to improve cumene conversion while maintaining the selectivity of CHP.

Research on developing comprehensive models for the cumene oxidation process remains limited. To the best of our knowledge, this process has only been studied in the literature [6]. The authors designed the process based on the kinetic expressions derived from their experimental data. Previous research has shown that appropriate process design and optimization can enhance conversion and selectivity while reducing the energy burden required [4]. In this paper, we propose an approach to minimize the use of utilities and capital costs in CHP production by eliminating inefficient cooling equipment and maximizing the potential of separators in the production process.

A comprehensive analysis of the physical and thermodynamic properties of the reactant and product mixtures is essential for developing an accurate process model. By employing appropriate estimation methods, such as the group contribution method and COSMO-based calculations, we can obtain more accurate kinetic parameters for the cumene oxidation reaction [7]. Additionally, designing more efficient reactor configurations, such as using dual-flow reactors or sequential reactor arrangements, can improve per-pass conversion and CHP yield while reducing the energy requirements for cooling. By adopting a more integrated and innovative approach, significant reductions in operational and investment costs can be achieved, making the CHP production process more sustainable and economical. Through in-depth analysis of process configurations and efficient control strategies, this article will explore the potential for cost savings and performance improvements in CHP production, contributing meaningfully to the development of a more environmentally friendly and sustainable chemical industry.

2. Methods

To enhance the efficiency of the cumene oxidation process, Aspen HYSYS V11 are used for simulation, design, optimization, and control. The system consists of eight components: α,α-dimethyl benzyl alcohol (DMBA), methyl phenyl ketone (AP), isopropyl benzene (cumene), formic acid (FA), cumene hydroperoxide (CHP), water (H_2O), acetone (ACT), and phenol (PHL). The non-random two-liquid (NRTL) model is applied for calculating mixture properties, the process follows Figure 1. The process starts with 30,000 kg/h of fresh cumene, which is combined with recycled streams to produce a total feed of 81,338 kg/h. This feed is sent to a biphasic CSTR operating at 375.4 K and 3.0 atm, achieving a cumene conversion of 33.1% per pass and a CHP yield of 29.7%. The reactor's optimized volume is 1620 m^3. Following the reaction, unreacted cumene is separated and recycled back to the reactor, while the liquid stream undergoes stripping for CHP purification. The stripper, operated at 0.095 atm, produces CHP with a purity of 82 wt%, suitable for further pyrolysis.

As a modification, the cooler between the CSTR and the separator is removed to evaluate differences in energy consumption between the original and modified processes. Key variables, such as reactor temperature and volume, cooler temperatures, air feed rate, are optimized using simulated annealing. This approach minimizes energy use while maintaining product quality. Additionally, further improvements in energy efficiency can be achieved by integrating heat recovery systems, as demonstrated through energy consumption comparisons.

3. Results and Discussion

3.1. Differences Between Basic and Modified Process

The cumene oxidation process was simulated for both the basic and modified methods using Aspen HYSYS V11. Figures 2 and 3 illustrate the simulation results and process flow diagram for

the basic method, while Figures 4 and 5 present the corresponding details for the modified method, while Table S1 (Supporting Information) present mass and energy balances of the modified process. In the basic process, a cooler is placed between the reactor (CSTR) and the separator to lower the temperature of the reactor effluent before separation. This configuration requires additional energy to operate the cooler. The unreacted cumene from the separator is then recycled back to the reactor, where it is mixed with fresh cumene feed in the mixer. The modified process eliminates the cooler between the reactor and the separator, allowing the reactor effluent to flow directly to the separator without cooling. This modification reduces energy consumption by removing the need for the cooling system. The unreacted cumene is recycled in the same manner as in the basic process. By comparing energy consumption, the modified process demonstrates greater efficiency through improved heat integration and a simpler process flow. This highlights its advantage in reducing energy requirements, while maintaining operational effectiveness. Meanwhile the chemical reactions follow as below:

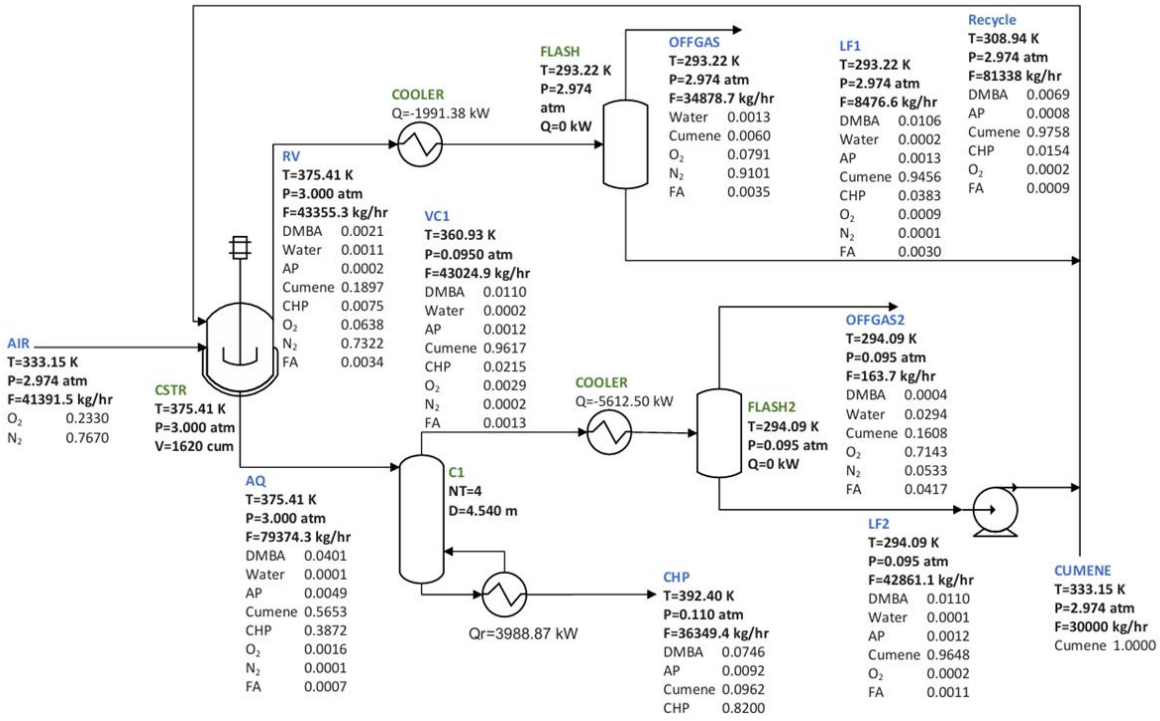

Figure 1. Basic process flow diagram of cumene hydroperoxide production [7]

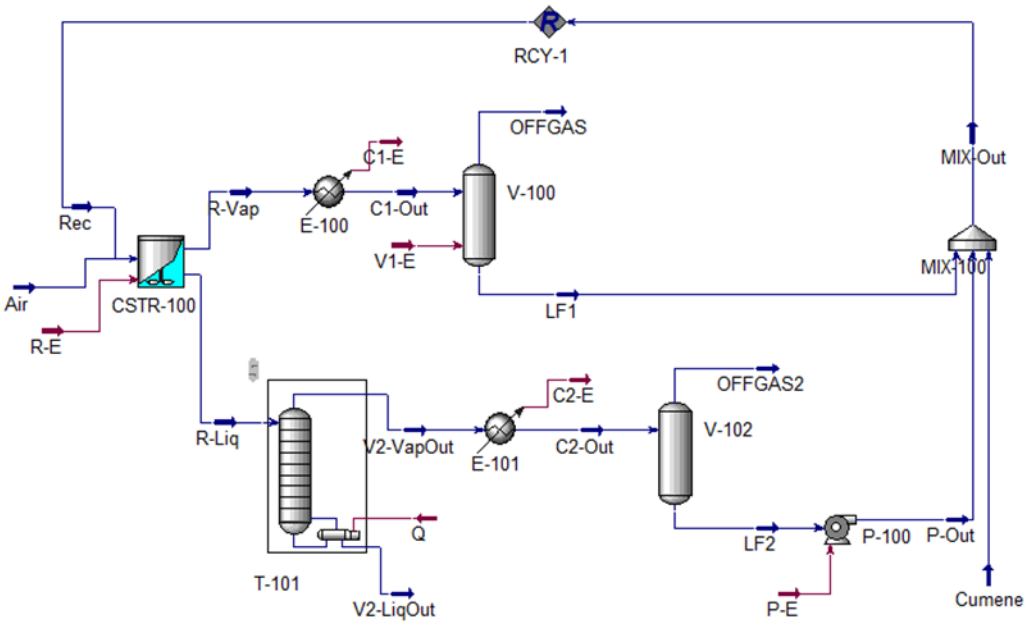

Figure 2. Aspen HYSYS simulation of the basic cumene hydroperoxide production

Chemical reactions [4]:

$C_9H_{12} + O_2 \rightarrow C_9H_{12}O_2$

$\Delta H_{reaction\ 1}$ = -82.4 kJ/mol

$C_9H_{12}O_2 \rightarrow C_9H_{12}O + 5O_2$

$\Delta H_{reaction\ 2}$ = -172 kJ/mol

$C_9H_{12}O_2 + O_2 \rightarrow C_8H_8O + CH_2O_2 + H_2O$

$\Delta H_{reaction\ 3}$ = -628.8 kJ/mol

Based on the calculation of the total reactions enthalpy (ΔH) at a temperature of 298 K, the result shows a negative ΔH value. Cause of that, it can be concluded that the ongoing reaction was an exothermic reaction that releases heat. The ΔG_f value for each component at a temperature of 298 K can be seen in Table 1 [13-15].

Calculation of ΔG_f Reaction (1):

$$\Delta G^\circ_{298} = \Delta G^\circ_{298(produk)} - \Delta G^\circ_{298(reaktan)}$$

$$\Delta G^\circ_{298} = (96\ kJ/mol) - (137.1 + 0\ kJ/mol)$$

$$\Delta G^\circ_{298} = -41.1\ kJ/mol$$

$$K_{298} = \exp(-\Delta G^\circ_{298}/RT)$$

$$= \exp\left(\frac{-(-41{,}100\ J/mol)}{8.314\ J/mol.K \times 298\ K}\right)$$

$$= 1.60 \times 10^7$$

At operating temperature of 375.41 K

$$ln\frac{K_{375.41}}{K_{298}} = \left[\left(\frac{-\Delta H^\circ_{298}}{R}\right) \times \left(\frac{1}{T} - \frac{1}{T_{298}}\right)\right]$$

$$ln\frac{K_{375.41}}{1.60 \times 10^7} = \left[\left(\frac{-(-82{,}400\ J/mol)}{8.314\ J/mol.K}\right) \times \left(\frac{1}{375.41} - \frac{1}{298}\right)\right]$$

$$\ln\frac{K_{375.41}}{1.60 \times 10^7} = -6.86$$

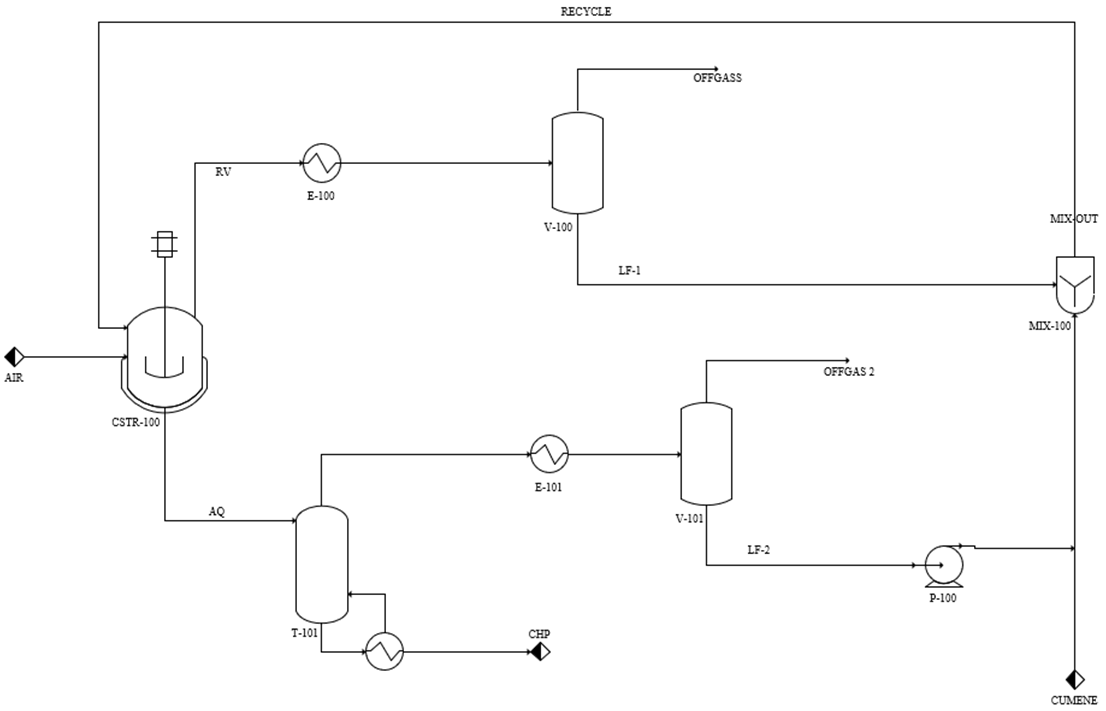

Figure 3. Process flow diagram of basic process [7]

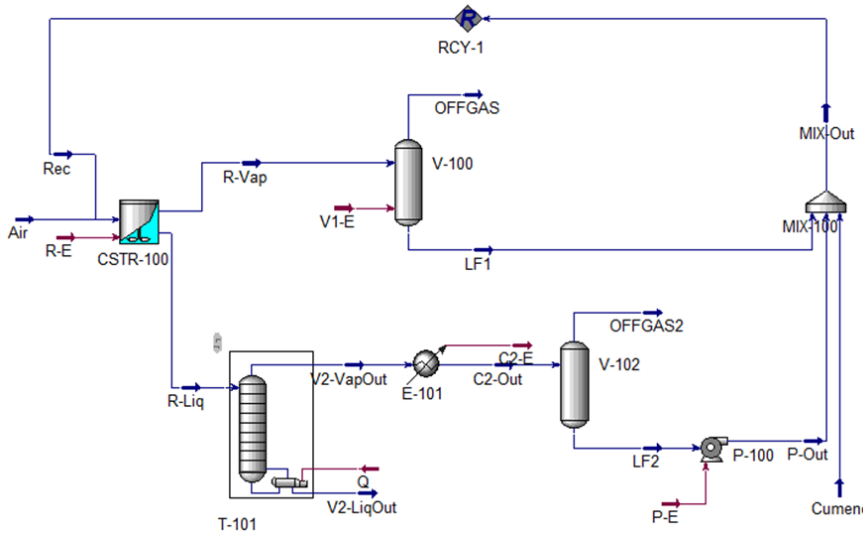

Figure 4. Aspen HYSYS simulation of the modified cumene hydroperoxide production

$K_{375.41} = 1.68 \times 10^4$

Because the value of $K_{375.41} > 1$, thus, the first reaction (main) is irreversible.

Calculation of ΔG_f Reaction (2):

$\Delta G°_{298} = \Delta G°_{298(produk)} - \Delta G°_{298(reaktan)}$

$\Delta G°_{298} = (3.33\ kJ/mol) - (96 + 0\ kJ/mol)$

$\Delta G°_{298} = -92.67\ kJ/mol$

$K_{298} = \exp(-\Delta G°_{298}/RT)$

$= \exp\left(\frac{-(-92{,}670\ J/mol)}{8.314\ J/mol.K \times 298\ K}\right)$

$= 1.75 \times 10^{16}$

At operating temperature of 375.41 K

$\ln\frac{K_{375.41}}{K_{298}} = \left[\left(\frac{-\Delta H°_{298}}{R}\right) \times \left(\frac{1}{T} - \frac{1}{T_{298}}\right)\right]$

$\ln\frac{K_{375.41}}{1.75 \times 10^{16}} = \left[\left(\frac{-(-448{,}270\ J/mol)}{8.314\ J/mol.K}\right) \times \left(\frac{1}{375.41} - \frac{1}{298}\right)\right]$

$\ln\frac{K_{375.41}}{1.75 \times 10^{16}} = -14.32$

$K_{375.41} = 1.05667 \times 10^{10}$

Because the value of $K_{375.41} > 1$, thus, the second reaction is irreversible.

Calculation of ΔG_f Reaction (3):

$\Delta G°_{298} = \Delta G°_{298(produk)} - \Delta G°_{298(reaktan)}$

$\Delta G°_{298} = (-1.27 + (-351) + 0)kJ/mol - (96 + 0)kJ/mol$

$\Delta G°_{298} = (-352.27)kJ/mol - (96)kJ/mol$

$\Delta G°_{298} = -448.27\ kJ/mol$

$K_{298} = \exp(-\Delta G°_{298}/RT)$

$= \exp\left(\frac{-(-448{,}270\ J/mol)}{8.314\ J/mol.K \times 298\ K}\right)$

$= 3.78 \times 10^{78}$

At operating temperature of 375.41 K

$\ln\frac{K_{375.41}}{K_{298}} = \left[\left(\frac{-\Delta H°_{298}}{R}\right) \times \left(\frac{1}{T} - \frac{1}{T_{298}}\right)\right]$

$\ln\frac{K_{375.41}}{1.60 \times 10^{7}} = \left[\left(\frac{-(-448{,}270\ J/mol)}{8.314\ J/mol.K}\right) \times \left(\frac{1}{375.41} - \frac{1}{298}\right)\right]$

$\ln\frac{K_{375.41}}{3.78 \times 10^{78}} = -37.31$

$K_{375.41} = 2.365724 \times 10^{62}$

Because the value of $K_{375.41} > 1$, thus, the third reaction is irreversible.

Therefore, the production of CHP ($C_9H_{12}O_2$) occurs in the first reaction (main reaction) that cumene (C_9H_{12}) oxidized by O_2 to CHP. The second reaction is the decomposition of CHP which produces by-products such as $C_9H_{12}O$ and oxygen. The third reaction shows the further oxidation reaction that occurs at the CHP to produce acetophenone (C_8H_8O), formic acid (CH_2O_2), and H_2O [4]. During oxidation, a small amount of organic acid is typically formed, which leads to CHP decomposition and consequently lowers its yield [16].

3.2. Comparison of Energy Efficiency before and after Modified Optimization

The net-energy required for both the basic and modified processes is shown in Table 2. In the basic process, the total energy required by the system is 265,992,099.05 kJ/h. The energy consumption is distributed across various units as follows: 10,364,892.77 kJ/h for the recycle cooler, 131,086,244.95 kJ/h for the product cooler, 35,882,021.84 kJ/h for the CSTR, -1,530.44 kJ/h for the separator, 88,532,262.41 kJ/h for the reboiler absorber, and 128,207.53 kJ/h for the pump. In contrast, the modified process, with the cooler between the CSTR and separator removed, has a total energy consumption of 245,259,223.09 kJ/h. The energy distribution is as follows:

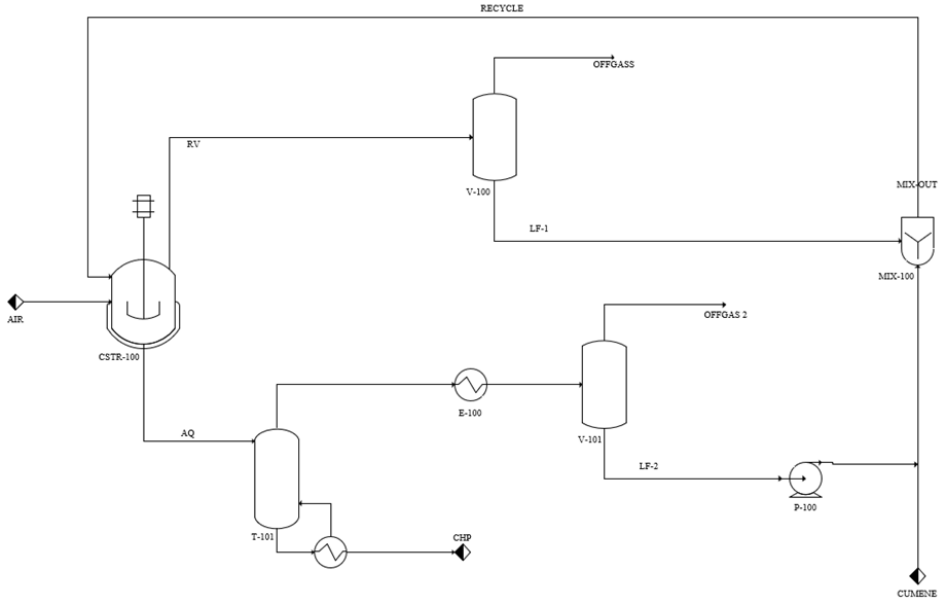

Figure 5. Process flow diagram of modified process

35,882,246.06 kJ/h for the CSTR, -10,366,416.94 kJ/h for the separator, 88,528,622.50 kJ/h for the reboiler absorber, 128,207.85 kJ/h for the pump, and 131,086,563.63 kJ/h for the product cooler. By removing the recycle cooler, the total energy required by the modified process is reduced by 20,732,875.95 kJ/h. This represents a significant improvement in the energy efficiency of the process, as energy consumption is lower in the modified configuration while maintaining system performance. This modification illustrates a more efficient process by redistributing the thermal load, eliminating the need for an additional cooler, and streamlining energy use across the system. As a result, the modified process has a better energy efficiency, closer to the ideal of minimizing unnecessary energy consumption, making it more sustainable and cost-effective than the basic process.

3.3. Evidence of Capital and Utilites Cost Savings from Cooler Removal in the Recycle System

The cost analysis for both the basic and modified processes indicates a notable difference in capital and utilities costs due to the removal of the cooler in the modified process and shown in Table 3, 4, and 5. For the basic process, the total capital cost is $7,463,410, with an operating cost of $10,425,200 per year. In contrast, the modified process shows a capital cost of $7,254,840, which is lower, while the operating cost is slightly

Table 1. Data ΔGf for each component at temperature 298 K

Compound Name	Molecular Formula	$G_{f\,298\,K}$ (kJ/mol)
Cumene	C_9H_{12}	137,1
Oxygen	O_2	0
Cumene Hydroperoxide	$C_9H_{12}O_2$	96
α,α dimethyl benzyl alcohol	$C_9H_{12}O$	3,33
Acetophenone	C_8H_8O	-1,27
Formic Acid	CH_2O_2	-351
Water	H_2O	0

Table 2. Comparison of energy required for basic and modified process

Energy Stream	Required Energy (kJ/h)	
	Basic Proces	Modified Process
R-E	35.882.021,84	35.882.246,06
V1-E	-1.530,44	-10.366.416,94
Q	88.532.262,41	88.528.622,50
P-E	128.207,53	128.207,85
C1-E	10.364.892,77	-
C2-E	131.086.244,95	131.086.563,63
Total	265.992.099,05	245.259.223,09

Table 3. Overall cost and sales comparison for basic and modified process

Cost Item	Amount of Cost (USD)		
	Basic Process	Modified Process	Savings
Total Capital Cost	7,463,410	7,254,840	208,570
Total Operating Cost/Year	10,425,200	10,313,300	111,900
Total Raw Material Cost/Year	0	0	0
Total Product Sales/Year	12,395,200	12,394,900	300
Total Utilites Cost/Year	8,305,180	8,201,600	103,580
Total	38,588,990	38,164,640	424,350

Table 4. Utilities cost comparison for basic and modified process

Cost Item	Amount of cost (USD/Year)		
	Basic Process	Modified Process	Savings
Electricity	156,035.20	156,035.20	0
Refregerant – Freon 12	1,409,400.76	1,303,937.26	105,463.50
Steam	6,738,556.80	6,738,556.80	0
Total	8,305,180	8,201,600	103,580

reduced to $10,313,300 per year. This results in an annual operating cost savings of approximately $111,900. In terms of equipment costs, the basic process requires $1,404,100 for equipment, compared to $1,384,400 in the modified process, resulting in a savings of $19,700 in equipment costs. Additionally, the installed cost for the basic process is $3,790,300, while the modified process has a total installed cost of $3,693,600, reflecting a reduction of $96,700. The utilities costs also show a significant difference between the two processes. The basic process incurs a utilities cost of $8,305,180 per year, while the modified process reduces this cost to $8,201,600 per year, saving $103,580 annually. This reduction can be attributed to the elimination of the cooler, which reduces the energy required for cooling and, therefore, lowers the electricity consumption and the need for refrigerant. Moreover, the modified process achieves lower utility costs in specific areas. For example, the cost of refrigerant (Freon 12) in the basic process is $160.83 per hour, while the modified process reduces this to $149.05 per hour. Similarly, the steam cost remains consistent across both processes, but the reduction in refrigerant and electricity usage further contributes to overall savings.

4. Conclusion

In conclusion, the modification of the cumene oxidation process by eliminating the cooler between the reactor and the separator demonstrates significant improvements in both energy efficiency and cost savings. The total energy required for the modified process is 245,259,223.09 kJ/h, which is 20,732,875.95 kJ/h lower than the basic process, which requires 265,992,099.05 kJ/h. This reduction in energy consumption results from the removal of the cooler, which lowers the overall energy demand while maintaining system performance. Additionally, the capital costs for the modified process are lower, with a reduction of $96,700 in installed costs and $19,700 in equipment costs. Operating costs are also reduced by $111,900 per year, and utilities costs decrease by $103,580 annually. The removal of the cooler leads to lower electricity and refrigerant consumption, further contributing to cost savings. Thus, the modified process is more energy-efficient, cost-effective, and sustainable compared to the basic process, highlighting its advantage in optimizing the cumene oxidation process.

CRediT Author Statement

Authors contributions: B. M. Marpaung was responsible for conceptualization, formal analysis, investigation, software development, visualization, writing, review and editing, as well as supervision. H. J. Setyanto contributed to conceptualization, methodology, visualization, writing, software development, review and editing, project administration, and validation. St. N. Aliyah handled data curation, formal analysis, validation, and writing, including review and editing, while also overseeing supervision tasks. Finally, L. C. E. Haryono focused on investigation, methodology, software development, visualization, writing the original draft, and conducting reviews and edits.

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Table 5. Equipment cost comparison for basic and modified process

Cost Item	Amount of Cost (USD)		
	Basic Process	Modified Process	Savings
Equipment Cost	1,404,100	1,384,400	19,700
Instaleed Cost	3,790,300	3,693,600	96,700
Total	5,194,400	5,078,000	116,400

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