

Reaction-Separation Process Integration and Working Fluid Optimization for Organic Rankine Cycles Recovering Waste Heat in Cumene Synthesis

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Reaction and distillation separation processes are two significantly energy-intensive unit operations in the chemical industry. Due to the high-temperature reaction and separation conditions, a large amount of waste heat with multiple grades is produced, which should be effectively utilized. In the article, the organic Rankine cycle (ORC) system is adopted to recover the waste heat in the reaction-separation process of cumene synthesis to generate electricity. The design parameters of the ORC system with eight working fluids including R113, R601, R123, R601a, R245ca, R245fa, R600 and R600a are optimized, aiming to maximize annual net economic revenues (NER) through the sequential quadratic programming (SQP). Simultaneously, the thermal efficiency (η_{ORC}) of ORC system with optimal economic performance is calculated for eight working fluids. The results illustrate that R113 performs better than other working fluids in terms of NER and η_{ORC} . The corresponding annual net electricity generation (NEG), annual NER of ORC system (NER_{ORC}) and overall process ($\text{NER}_{\text{overall}}$) and η_{ORC} can reach 620.83 kW, 0.75×10^5 \$/y, 2.11×10^5 \$/y and 21.79 %.

1. Introduction

Reaction and subsequent distillation separation processes are often encountered in the chemical industry and extensively studied. Yu and Chien (2017) investigated the steady state design and process parameters optimization of ethylene glycol (EG) production process by the dimethyl oxalate hydrogenation. Inspired by this work, Wei et al., (2018) proposed an improved overall process in 200 kt/a EG production using syngas to enhance production efficiency and decrease energy consumption. Yu et al. (2018) firstly developed the rigorous process design and parameters optimization for the complex and plant-wide dimethyl oxalate synthesis process from syngas. Luyben (2010) studied the reaction and separation process of methanol production using syngas in the perspective of economy and controllability. Subsequently, Luyben (2011) investigated the process of synthesizing butyl acetate using methyl acetate and butanol in terms of process parameters optimization and robot plantwide control structure establishment. An inherent fact should be noted in the reaction-separation process that a large amount of waste heat with multiple grades is produced due to the high-temperature reaction and separation conditions. Up to now, most of the previous investigations focused on the process design, process optimization, parameters adjustment and single feed-effluent Heat Integration for the reaction-distillation separation process but neglected the recovery of the waste heat.

The waste heat in the reaction-separation process should be utilized reasonably and efficiently from the perspective of economic efficiency and environmental sustainability. The current researches indicate that organic Rankine cycle (ORC) is an effective technique for recovering heat, which can convert low-grade waste heat into high-grade and clean electricity via using low-boiling organic compounds as working fluids (Yu et al., 2019). Up to now, a considerable amount of existing literature focuses on the basic theoretical research of ORC system, for example, the selection of working fluids (Bao and Zhao 2013), thermodynamic (Vélez et al., 2012) and economic performance (Tchanche et al., 2011) or equipment hardware (Lecompte et al., 2015). However,

there are only a limited number of studies on the recovery and reuse of waste heat for a specific and detailed process via ORC technology. Gao et al. (2018) investigated the mechanical vapor recompression heat pump (HP) distillation coupled with ORC process via taking the separation of the benzene-toluene mixture as an example. Li et al. (2019) proposed a novel economizer and ORC assisted extractive distillation process to recover both latent and sensible waste heat for the separation of n-heptane/isobutanol azeotrope with n-methyl-2-pyrrolidone as a solvent. Yang et al. (2019) proposed the HP assisted reactive dividing-wall column combining with ORC configuration to effectively convert the waste heat to clean electricity for the diethyl carbonate synthesis process. Liu et al. (2020) proposed and optimized a novel superstructure of the integration of methanol-to-gasoline process with ORC in the hope of improving energy efficiency. However, the valuable insights into waste heat recovery of the reaction-separation processes are still rare and none of the studies focused on the reaction-separation process of cumene (Ce) synthesis.

In this study, the waste heat recovery of the reaction-separation process is investigated by the ORC system to promote economic efficiency and environmental sustainability. First, the reaction-separation process for producing Ce is simulated based on the work of Luyben (2011). Secondly, the ORC assisted reaction-separation process is proposed to recover waste heat and enhance thermal efficiency. Simultaneously, R113, R601, R123, R601a, R245ca, R245fa, R600 and R600a are selected as alternative working fluids to drive ORC system. The optimization of ORC system with various working fluids are carried out via the sequential quadratic programming (SQP) with the maximum annual net economic revenue (NER) as the target. Thirdly, the thermal efficiency of the ORC system (η_{ORC}) with various working fluids are calculated. Finally, the working fluid with economic efficiency and environmentally friendly is identified for the ORC system assisted reaction-separation process of Ce synthesis.

2. Methodology

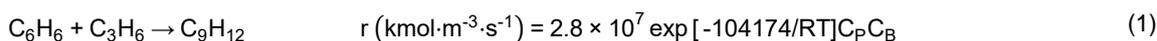
A systematic methodology of the waste heat recovery for producing cumene (Ce) in the reaction-separation process via the organic Rankine cycle (ORC) system is proposed and carried out. In this work, the conceptual methodology consists of five steps, as follows:

- (1) The existing reaction-separation process for producing Ce is repeated as the base case, while is compared with that in the literature (Luyben 2011).
- (2) The ORC assisted reaction-separation process is proposed to recover waste heat.
- (3) Several alternative working fluids including R113, R601, R123, R601a, R245ca, R245fa, R600 and R600a are selected for the proposed ORC system.
- (4) The ORC system with various working fluids are optimized via the sequential quadratic programming (SQP) with the maximum net economic revenue (NER) as target and the corresponding ORC thermal efficiency (η_{ORC}) are calculated.
- (5) The comparison of various working fluids is performed to determine the optimal working fluid for the ORC system assisted reactive-separation process of Ce synthesis.

3. Design basis

3.1 Description of reactive-separation process

The Ce (C_9H_{12}) can be synthesized through propylene (C_3H_6) and benzene (C_6H_6), which has been described in the reported literature (Luyben 2011). The overall production of Ce reaction involves the main reaction and an unwanted side reaction. In the reaction process, Ce product is produced via the reaction of propylene and benzene, and the product Ce is reacted further with propylene to produce the unwanted by-product p-diisopropyl benzene ($\text{C}_{12}\text{H}_{18}$, PDIB). The detailed reaction equations and individual corresponding kinetics are shown in Eq(1) and Eq(2). The units of reaction rates are $\text{kmol}\cdot\text{m}^{-3}\cdot\text{s}^{-1}$, the units of activation energy (E) are kJ/kmol , and the [Ci] basis is molarity. Simultaneously, the reaction is carried out in the vapour phase in the presence of a solid catalyst. The void fraction and solid density are assumed to be 0.5 and $2,000\text{ kg}/\text{m}^3$.



In the process, the feed conditions, equipment sizes, operation conditions are the same as the Luyben's work (Luyben 2011). Figure 1a shows the reaction-separation flowsheet of the Luyben's work (Luyben 2011) with detailed material, energy information and operation parameters. The fresh feed streams of benzene and mixed C3 (propylene and propane) enter the process as liquids. The fresh feed flowrates of the C3 stream is set at $101.93\text{ kmol}/\text{h}$ with the composition of 95 mol% propylene and 5 mol% propane and the fresh feed of benzene

is 98.78 kmol/h. The fresh feed streams are combined with a liquid recycle stream (D1) and fed into the vaporizer. The operation temperature and pressure of the vaporizer are 210 °C and 25 bar. The liquid stream is vaporized into saturated gas, and then the saturated gas is preheated in two heat exchangers before entering the reactor. The first one recovers heat from the hot reactor effluent (358.5 °C) and the second one adds additional heat to bring the reactor inlet temperature up to 358 °C. The reactor is a cooled tubular reactor containing 1,500 tubes, 0.0763 m in diameter and 6 m in length that generates high-pressure steam from the exothermic reactions. The temperature in the steam side of the reactor is 358 °C and the overall heat transfer coefficient of $0.065 \text{ kW m}^{-2} \text{ °C}^{-1}$ is used. The reactor effluent leaves at 358.5 °C is cooled to 279 °C in the feed-effluent heat exchanger (FEHE) and sent to a condenser (HX2) in which it is cooled to 90 °C using cooling water. And then, the two-phase stream from the condenser is fed into the flash tank. The gas from the flash tank is used as fuel and the liquid is fed into the first distillation column (C1). The C1 has 15 stages and the feed location is 8th tray. The reflux ratio (RR_1) is 0.44 and the benzene composition in the bottom (B1) is specified as 0.05 mol% via adjusting the distillate rates (D1). The B1 is fed into the second distillation column (C2) with 20 stages from the 12th tray. The Ce purity in the D2 stream and B2 stream are specified as 99.9 mol% and 0.1 mol% via adjusting RR_2 and D2 flowrates. The units of duty are Gcal/h.

The NRTL physical property package is used in the Aspen (V11) simulations (Luyben 2011). Figure 1b shows the self-made simulation results of reaction-separation process for producing Ce. It can be seen that the simulation results show a slight difference caused by software version, convergence methods, and pressure drop, compared to Luyben's work (Luyben 2011).

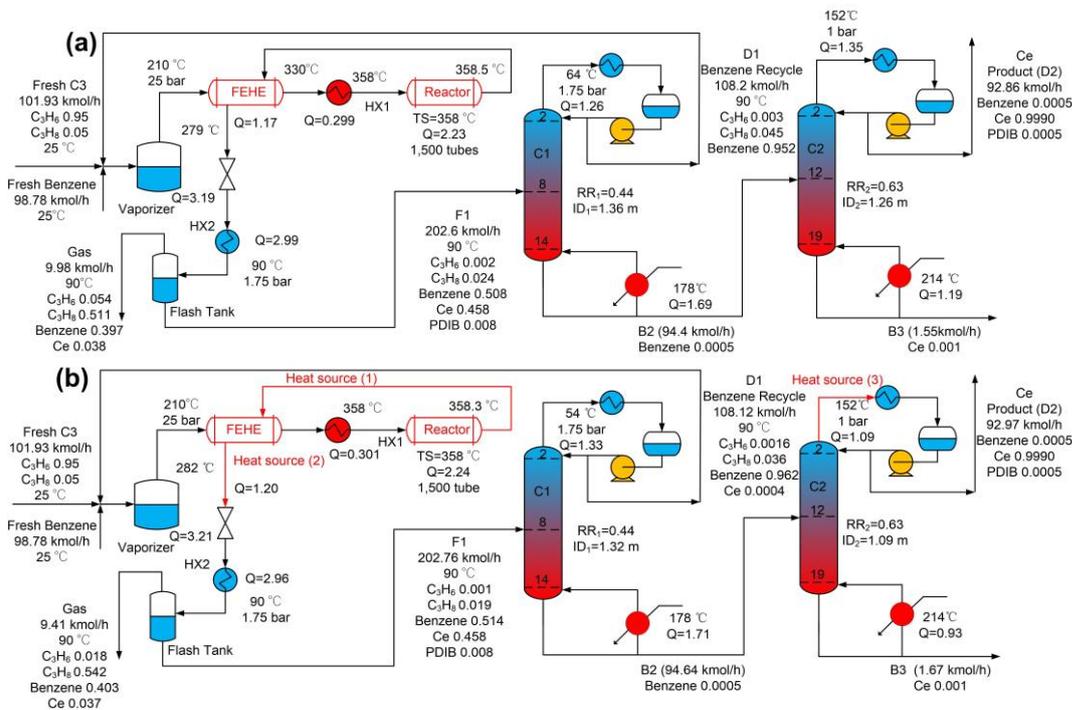


Figure 1: The reaction-separation process for producing Ce (a) Existing (b) Self-made

3.2 Selection of working fluids

Figure 2 illustrates the basic ORC system diagram composed of evaporator, turbine, condenser and pump. Simultaneously, four thermodynamic processes including of isobaric heating (1→2), isentropic expansion (2→3), isobaric cooling (3→4) and isentropic compression (4→1) occur in the evaporator, turbine, condenser and pump. The waste heat source is introduced in the evaporator to drive the ORC system, and three streams can be used as the heat source in the overall process of producing Ce. The heat source 1 and heat source 2 are the streams from the outlet of the reactor and the FEHE, and the heat source 3 is the vapour stream at the top of the distillation column (C2). In the ORC system, the electricity can be generated and consumed in the turbine and pump. In the work, only the heat source 2 is investigated, without considering the influence of process parameters (i.e. reactor size, reactor inlet temperature, the quantity of heat transfers in the FEHE) on ORC system. The Peng Robinson (PR) property method is adopted during the ORC loop simulation (Gao et al.,

2018). Generally, mechanical efficiency and isentropic efficiency are between 0.85 and 0.95. In the paper, the isentropic and mechanical efficiencies of the turbine are assumed to be 0.9 and 0.9.

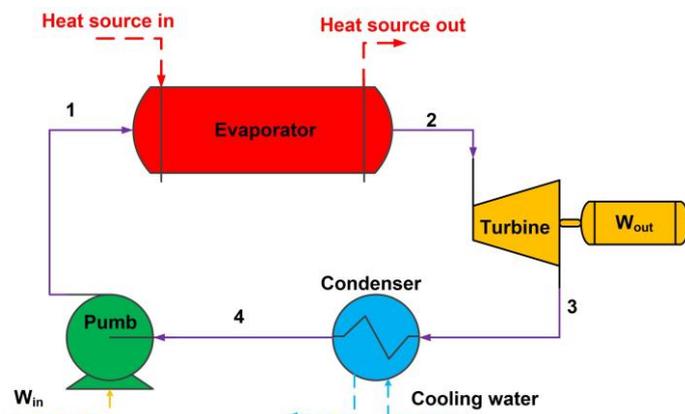


Figure 2: The flowsheet of a basic ORC system

The selection of the feasible working fluids is the first step to implement ORC system. In this study, eight working fluids are investigated based on thumb rules provided by predecessors, for example, the relationship between work fluids critical temperature and heat source temperature (Satanphol et al., 2017). Table 1 lists the eight alternative working fluids in order of normal boiling points. Other properties such as critical temperature, critical pressure and the environmental, health, and safety indexes are also demonstrated (Yang et al., 2019).

Table 1: Physical properties of selected working fluids

Working fluids	R113	R601	R123	R601a	R245ca	R245fa	R600	R600a
Chemical formula	$\text{CCl}_2\text{FCClF}_2$	C_5H_{12}	CHCl_2CF_3	C_5H_{12}	$\text{CH}_2\text{FCF}_2\text{CHF}_2$	$\text{CF}_3\text{CH}_2\text{CHF}_2$	C_4H_{10}	C_4H_{10}
CAS No	76-13-1	109-66-0306-83-2	78-78-4679-86-7	460-73-1	106-97-875-28-5			
Boiling point (°C)	47.6	36.07	27.90	27.84	25.25	15.3	-0.5	-11.72
Critical temperature (°C)	214.10	196.55	183.79	187.25	174.42	154.05	151.97	134.65
Critical pressure (bar)	34.10	33.70	36.76	33.80	39.25	36.40	37.96	36.40
ODP	0.85	0	0.01	0	0	0	0	0
GWP (100 y)	6,130	20	77.00	20	726	1,050	20	20

3.3 Optimization objective and method

In this work, only the parameters of ORC system are optimized to maximize the NER. The NER consists of the total capital costs and the energy costs generated or consumed for ORC system. The total capital costs are made of the heat exchangers costs (condenser and evaporator) and the turbine costs, and the pump costs are ignored due to the lower costs, while the payback period is assumed to be 3 years. The energy costs include net electric generation (NEG) costs and cooling water costs. The electrical energy is consumed in the pump and generated in the turbine, while the cooling water costs are consumed in the condenser. The costs of the HX2 and the corresponding cooling water costs required are replaced by the ORC system for the overall reaction-separation process. The operating time is assumed to be 365×24 h (Luyben 2013). Table 2 illustrates the detailed formulas and parameters for economic optimization (Luyben 2011) and the calculation formula of turbine cost is derived from the work of Luo et al. (2015).

The complete process optimization model based on the SQP solver is adopted to optimize the ORC system and to determine the operating parameters in Aspen Plus. For the ORC system, the optimization variables are the flowrates of working fluids (F_{WF}), the pump discharge pressure ($P_{pump-out}$), the pressure ratio of the turbine (P_r), and the degree of superheating of the working fluids at the evaporator exit (T_{SPH}). The optimization is carried out in the sub-critical region of the working fluids, and the critical pressure is taken as the upper bound of the $P_{pump-out}$. The lower bound of the T_{SPH} is specified as 1 °C to avoid any discontinuities which may arise at the vapour-liquid phase boundary during optimization. Simultaneously, several constraints are performed during optimization, as follows (Satanphol et al., 2017):

(1) The outlet temperature of heat source is specified to be greater than or equal to 90 °C to ensure the consistency of subsequent material and energy information with Luyben's work (Luyben 2011);

- (2) The minimum allowable pressure at the turbine exit is specified as 5 kPa;
 (3) The outlet temperature of the condenser is required to be no less than 30 °C to ensure the working fluids in the condenser can be cooled with cooling water.

Table 2: The formulas and parameters used for economic optimization

Parameters	Formula or data	Units
Condenser:		
Heat transfer coefficient (U_C)	0.852	kW/(°C·m ²)
Temperature difference (ΔT)	13.9	°C
Heat transfer area (A_C)	$Q_C / (U_C \times \Delta T)$	m ²
Capital cost	$7,296 \times A_C^{0.65}$	\$
Evaporator		
Heat transfer coefficient (U_R)	0.568	kW/(°C·m ²)
Temperature difference (ΔT)	34.8	°C
Heat transfer area (A_R)	$Q_R / (U_R \times \Delta T)$	m ²
Capital cost	$7,296 \times A_R^{0.65}$	\$
Turbine costs	$1,536.8 / 280 \times 664.1 \times 1.15 \times (TW)^{0.82}$	\$
Electricity price	0.1	\$/ (kW·h)
Cooling water price	0.354	\$/GJ
Payback period	3	y
NER	(Total capital costs / Payback period) + annual energy costs	\$/y

4. Result and discussions

Table 3 summarizes the optimization variables and optimization results of the ORC with various working fluids. Simultaneously, the corresponding η_{ORC} calculated via the enthalpy of working fluids is also illustrated in Table 3. It can be seen that the different amounts of electricity can be generated for eight working fluids. The working fluid with the maximum NEG is R113, which can produce 620.83 kW and can generate 45.21 kW, 24.61 kW, 80.27 kW, 76.26 kW, 1,120.17 kW, 125.81 kW, 178.07 kW more than others working fluids (R601, R123, R601a, R245ca, R245fa, R600 and R600a).

Table 3: The optimization variables and optimization results of the ORC with various working fluids

	R113	R601	R123	R601a	R245ca	R245fa	R600	R600a
F_{WF} (kmol/h)	204.40	238.23	220.99	247.99	227.26	250.02	299.26	334.30
T_{SPH} (°C)	52.63	21.53	93.18	26.95	53.91	57.91	55.36	55.45
Pr	0.0168	0.0243	0.0309	0.0349	0.0311	0.0500	0.0752	0.1131
$P_{pump-out}$ (bar)	33.00	33.50	35.50	32.00	39.00	35.50	37.50	35.50
TW (kW)	661.54	620.66	637.53	584.77	588.24	543.77	546.52	495.53
PP (kW)	40.71	45.04	41.31	44.21	43.67	43.11	51.50	52.74
NEG (kW)	620.83	575.62	596.22	540.56	544.57	500.66	495.02	442.79
NER _{ORC} (10 ⁵ \$/y)	0.75	0.49	0.62	0.31	0.33	0.10	0.04	-0.24
NER _{overall} (10 ⁵ \$/y)	2.11	1.85	1.97	1.67	1.69	1.45	1.39	1.11
η_{ORC} (%)	21.79	20.23	20.93	19.07	19.19	17.61	17.44	15.62

There is a trade-off between the electricity benefits of ORC and the costs of ORC itself, it can be seen that the ORC with working fluids involved can generate different degrees of NER_{ORC}, except for R600a. However, all working fluids can bring large NER_{overall} since the costs of HX2 and corresponding cooling water can be avoided for the overall reaction-separation process with ORC system. The best economy is still working fluid R113, which is 1.00×10^5 \$/y away from the worst R600a for the NER_{overall}. The η_{ORC} of various working fluids is between 15.62 % and 21.79 %, the η_{ORC} of R113 working fluid is the highest, while that of R600a is the lowest. However, R113 is detrimental to environmental sustainability due to the highest GWP and ODP.

5. Conclusions

In this paper, the waste heat existing in the reaction-separation process for the synthesis of Ce product is recovered and utilized by introducing an ORC system. Eight working fluids including R113, R601, R123, R601a, R245ca, R245fa, R600 and R600a are investigated and optimized via SQP procedure with the maximum NER of ORC system as the target. Subsequently, the corresponding η_{ORC} of various working fluids is calculated for

the individual ORC system with optimal economic performance. The results show that the optimal working fluid is R113 among the eight working fluids in terms of NEG and NER, which can produce NEG of 620.83 kW/h, NER_{ORC} of 0.75×10^5 \$/y and $NER_{overall}$ of 2.11×10^5 \$/y. The η_{ORC} of working fluid R113 reaches up to 21.79 %, which is still the highest among the eight working fluids. However, the R113 has the highest GWP and ODP compared to other working fluids, which has a negative impact on the environment to some extent.

In the paper, the waste heat recovery only focused on the heat source in the reaction process, without investigating the heat source of the separation process. The waste heat recovery is carried out independently on the existing reaction-separation process, without considering the influence of the introduction of ORC on the parameters of the overall reaction-separation process. These two contents should be investigated in the future.

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