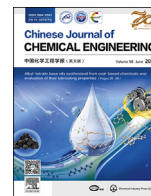




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Modeling and analysis of air combustion and steam regeneration in methanol to olefins processes

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ABSTRACT

Light olefins is the incredibly important materials in chemical industry. Methanol to olefins (MTO), which provides a non-oil route for light olefins production, received considerable attention in the past decades. However, the catalyst deactivation is an inevitable feature in MTO processes, and regeneration, therefore, is one of the key steps in industrial MTO processes. Traditionally the MTO catalyst is regenerated by removing the deposited coke *via* air combustion, which unavoidably transforms coke into carbon dioxide and reduces the carbon utilization efficiency. Recent study shows that the coke species over MTO catalyst can be regenerated *via* steam, which can promote the light olefins yield as the deactivated coke species can be essentially transferred to industrially useful synthesis gas, is a promising pathway for further MTO processes development. In this work, we modelled and analyzed these two MTO regeneration methods in terms of carbon utilization efficiency and technology economics. As shown, the steam regeneration could achieve a carbon utilization efficiency of 84.31%, compared to 74.74% for air combustion regeneration. The MTO processes using steam regeneration can essentially achieve the near-zero carbon emission. In addition, light olefins production of the MTO processes using steam regeneration is 12.81% higher than that using air combustion regeneration. In this regard, steam regeneration could be considered as a potential yet promising regeneration method for further MTO processes, showing not only great environmental benefits but also competitive economic performance.

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1. Introduction

Light olefins are important platform chemicals widely used in petrochemical industries [1]. Methanol-to-olefins (MTO) process is a significant approach to synthesize ethylene and propylene using non-oil feedstocks. The first methanol-to-olefins unit was built and commissioned in 2010 based on the dimethyl ether/methanol-to-olefins (DMTO) technology by Dalian Institute of Chemical Physics of Chinese Academy of Sciences [2,3]. As of the end of 2022, a total of 31 DMTO units had been licensed and 16 DMTO units had been started up and put into operation [4]. Therefore, the MTO process is expected to become a primary route for producing light olefins in the near future. One of the features of MTO processes is

that the use of SAPO-34 zeolite catalyst, which could be rapidly deactivated due to coke deposition. Thus, it is crucial to recover the activity of catalysts by a so-called catalyst regeneration process [5].

In MTO process, the catalyst regeneration is traditionally carried out *via* the combustion of coke in the air [6–8]. Jiang *et al.* [9] used H-SAPO-34 catalyst with synthetic air (20% (vol) oxygen) at 400 °C and 500 °C to a removal of up to 90% of organic deposits. Nan *et al.* [10] studied the kinetics of coke combustion on SAPO-34 in the MTO process based on the industrial data. They discovered that the coke retained in the regenerated catalyst is helpful to shorten or distinguish the induce period of MTO reaction, which provides guidelines to control coke combustion density and average coke content in MTO reactor. Xu *et al.* [11] investigated the regeneration conditions (at the temperature of 600, 620, 650, and 700 °C and regeneration time 50 min) to recover the spent DMTO catalyst in industrial fluidized bed reactor by air combustion process and studied the kinetics of air combustion in the DMTO catalyst. In

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a conventional industrial MTO unit, a fluidized bed reactor–regenerator system will be used because the catalyst would be readily deactivated by coke deposition in methanol conversion process. The deactivated catalyst from reactor will be continuously transported to regenerator in which the activity of catalyst will be recovered by burning the coke deposited on catalyst with air. The regenerated catalyst will then be circulating back to reactor for methanol conversion. As Li *et al.* [12] pointed out, coke plays a significant role in catalyst activity affecting the reaction kinetics, product selectivity, and methanol conversion in the MTO process. Normally a partial regeneration will be implemented in MTO regenerator as a small fraction of coke left on the catalyst would favor the selectivity of light olefins during methanol conversion owing to the shape-selectivity of zeolite type of catalyst. In addition to that, the coke (or activity) will manifest a certain distribution, which can theoretically be described by population balance model [12,13], because of the circulation of catalyst between fluidized bed reactor and regenerator.

In commercial applications regenerating deactivated catalysts with air combustion has been most frequently used [14–16]. However, air combustion regeneration process is a high exothermicity that can easily cause afterburn in MTO regenerator which might result in catalyst degradation. In addition, air combustion of the coke, despite releasing large amount of CO₂, will meantime remove the active species favoring light olefins formation in the catalyst and reduce the carbon utilization efficiency [17]. Therefore, to develop an efficient yet environment-friendly regeneration route is highly demanded in MTO process development.

Recently Zhou *et al.* [18] proposed that partial regeneration of spent SAPO-34 catalyst by steam can selectively transform the deactivated coke into hydrocarbon pool species (HCPs) to boost the light olefins selectivity. In this method, the majority of deposited coke formed in the reactor can be transformed into active coke species in the regenerator. The active coke species will remain in the catalyst particles and be circulated to the reactor to significantly promotes the ethylene and propylene selectivity in MTO processes. As most of coke formed in reactor will be kept after regeneration, which can greatly reduce the coke yield in the MTO reactor–regenerator system. Only a small portion of coke will be converted to flue gas in the regenerator and be released out of the MTO reactor–regenerator system. The flue gas is composed of carbon monoxide and hydrogen, namely syngas, and can be used as raw materials for the light olefins production. It is shown that the flue gas will consist of more than 88% high-value syngas and about 5% carbon dioxide in the steam regeneration approach. This opens an interesting way for MTO regeneration as it not only recovers the activity of catalyst with the boosting light olefins selectivity but also significantly reduces CO₂ emission with the enhanced carbon utilization efficiency [19].

SAPO-34 zeolites, known for their CHA structure and small 8-ring windows, are highly regarded as promising catalysts due to their ability to achieve selectivity to light olefins exceeding 80% in MTO processes [2]. The mechanism of MTO reactions with SAPO-34 zeolites is complex. Recent studies [20,21] indicate that light olefins production in the MTO process follows a dual-cycle reaction mechanism. Methanol is converted into light olefins during the olefin-based cycle, while the aromatic-based cycle involves the production of aromatic species through olefins aromatization, creating new active centers. In the MTO process, when the catalyst is going to deactivate, the main compounds of coke species are essentially the polycyclic aromatics [22,23] which may result in the coverage of acid sites [24,25] and blockage of nanopores in catalyst. After steam regeneration, most of the polycyclic aromatics will be cracked into the low-cyclic aromatics such as methylated benzenes and methylated naphthalene. These methylated benzenes

with fewer methyl groups, which will essentially have retained inside the zeolite catalyst, have been identified as active species, promoting ethylene formation *via* the aromatic-based cycle over SAPO-34 catalysts [26]. A small fraction of polycyclic aromatics (less than 30%) will be converted to CO and H₂ as by-products in the steam regeneration. Steam regenerated SAPO-34 zeolite catalyst, as shown in the previous study, can achieve 87% selectivity for light olefins in MTO reaction [18]. In fact, steam regeneration resolved the issue of coverage of acid sites and blockage of nanopores, thereby releasing free active sites instead of the generation of new acid sites. This process enhances the accessibility of free acid sites and increases the quantity of active coke, consequently leading to the improved catalytic performance [27].

Steam is prone to attacking the Al–O bond of the zeolite crystals such as ZSM-5, β, and HY zeolites under high temperature in presence of water [28–30], which indeed leads to the dealumination. However, SAPO-34 zeolites have much better hydrothermal stability than the zeolites mentioned above. It was discovered by Watanabe *et al.* [31] that SAPO-34 zeolites can withstand hydrothermal condition up to 1000 °C in almost pure steam. Liu *et al.* [32] reported that the SAPO-34 zeolite crystal structure was well preserved even after treatment with 100% steam at 800 °C for 24 h. In real MTO industrial units, the regeneration is normally conducted at 650–700 °C with air combustion, and the degrading of SAPO-34 zeolites has not been found. In fact, we did not find any problems concerning the hydrothermal stability in our pilot experiments with steam regeneration.

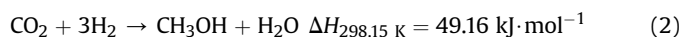
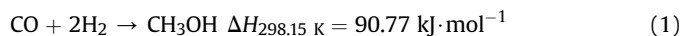
In this work, to study the feasibility of MTO processes using steam regeneration (MTO-SR), we modelled and analyzed MTO-SR and compared it with the MTO processes using air combustion regeneration (MTO-ACR) by using of the software package Aspen Plus V11. Specifically, we analyzed and evaluated both processes in terms of carbon utilization efficiency as well as techno-economic performance. In doing so, four performance indicators, *i.e.*, carbon utilization efficiency, energy efficiency, CO₂ emissions, and economic performance of light olefins production are considered according to the model we established (shown in Fig. 1).

2. Process Description and Modeling

The layouts of proposed processes, *i.e.*, MTO-ACR and MTO-SR, are respectively shown in Figs. 2 and 3. The processes considered in this work includes methanol synthesis (MS), methanol distillation (MD), MTO, olefins distillation (OD), and regeneration units (RU). RU can be based on either air combustion or steam regeneration.

2.1. MS and MD units

The purified syngas is intermingled with the flue gas generated in the regeneration process. The data presented in Table 1 compares the components for purified syngas as feedstocks and the data presented in the literature. After two times of pressurized flash evaporation, the water was removed from the mixed gas of purified syngas and circulating gas as shown in Fig. 3. The mixed syngas was pressurized to 5.0 MPa in the compressor C103, and then preheated to 200 °C by the preheater H101 before entering the synthesis reactor MS for reaction. The major reactions occur in the synthesis reactor in the Cu/Zn/Al/Zr catalyst [33].



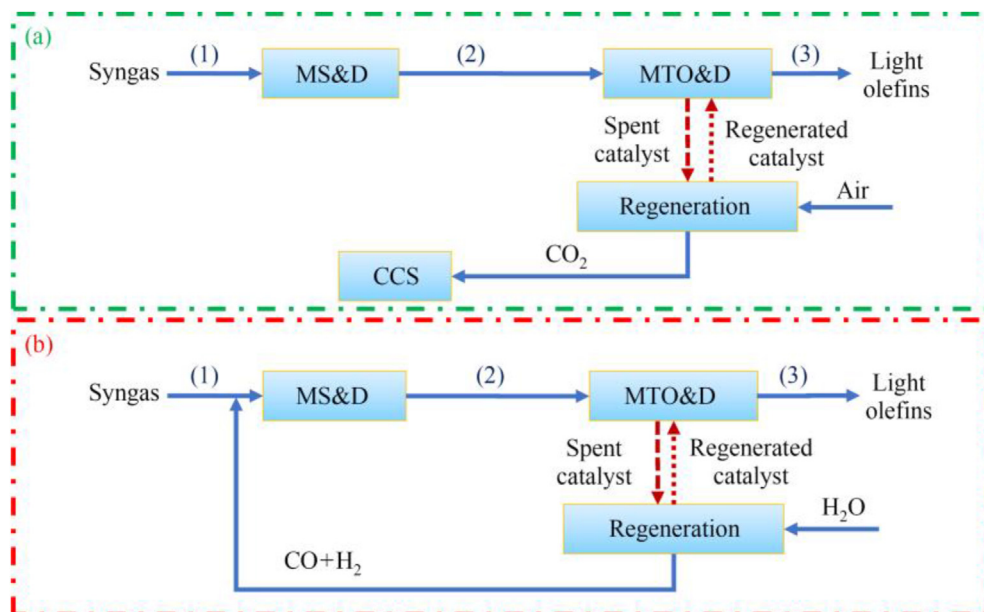


Fig. 1. The MTO processes with different regeneration routes: (a) MTO-ACR; (b) MTO-SR.

The gas from the synthesis reactor is cooled to 40 °C by the cooler H102, and then sent to the flash tank F103 to separate the unreacted syngas. The crude methanol separated from the flash tank F103 is sent to the rectification section. The distillation column

T401 was composed of 18 column plates, and the distillation column T402 was composed of 26 column plates. After two times of distillation of crude methanol, 99.99% (mass) methanol was obtained.

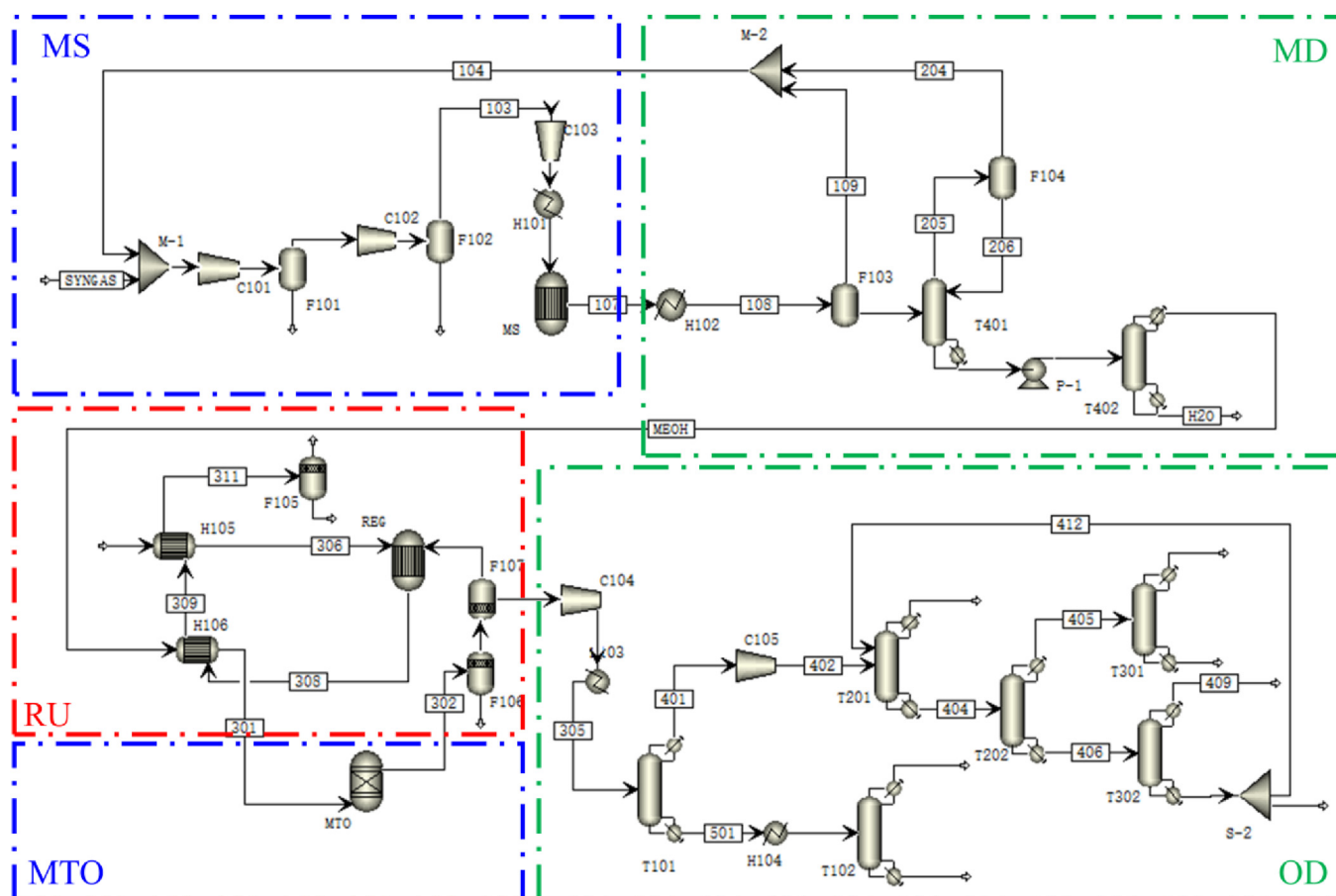


Fig. 2. Diagram of the MTO-ACR

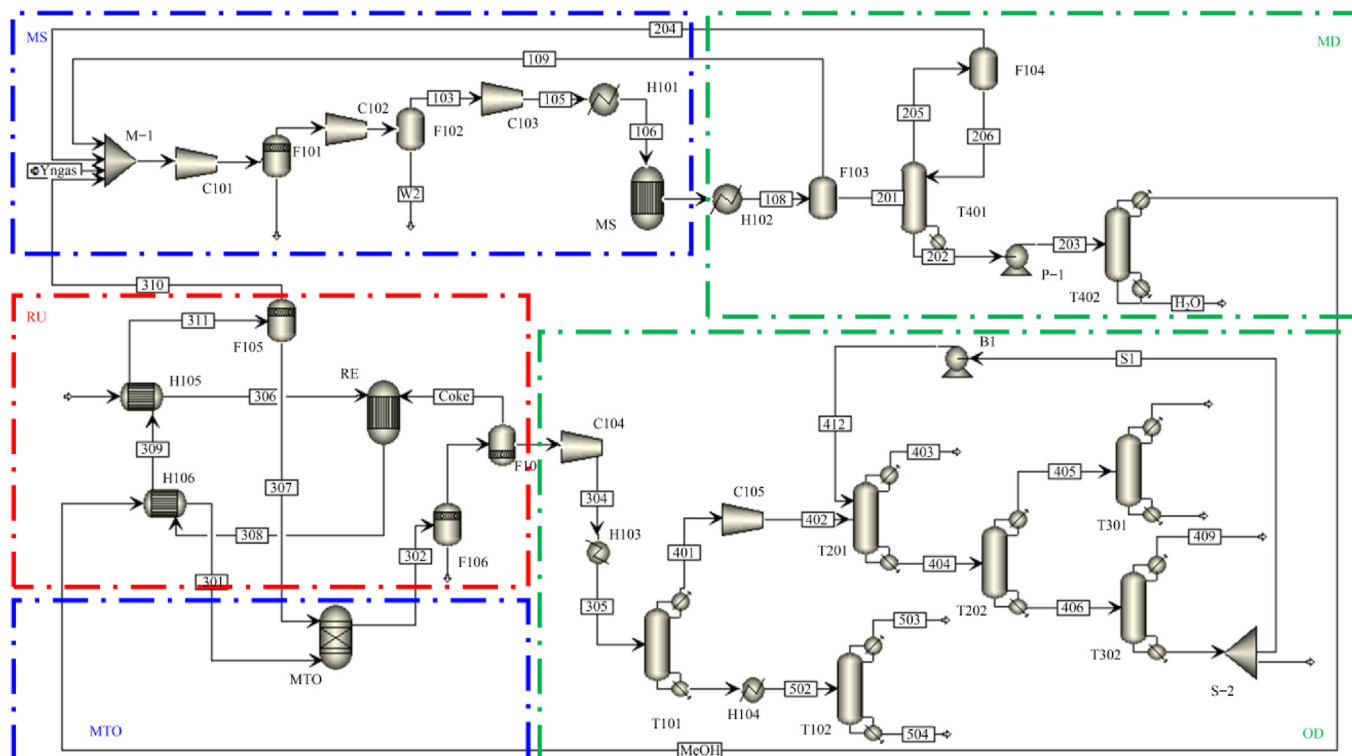


Fig. 3. Diagram of the MTO-SR

Table 1

Comparison for purified syngas: comparison between simulation data and industrial data [34]

Components/% (mol)	Industrial data	Simulation data
H ₂	0.6802	0.6903
CO	0.2724	0.2703
CO ₂	0.0394	0.0355
CH ₄	0.0024	0.0021
N ₂	0.0040	0.0023
CO + H ₂	0.9526	0.9606

A stoichiometric (Rstoc) model was used for reactor MS, Flash model was used for flash tank, and RadFrac model was used for rectification tower. The production rate of methanol was 1.8 million tons per year, the capacity of a typical MTO plant in China [35,36].

2.2. MTO and OD units

The unit is established based on DMTO technology. The schematic diagram of methanol to olefins processes and olefin distillation is shown in Fig. 3. In this section, the RKS-BM property method is selected [37,38]. The Ryield model can be used to simulate the synthesis of olefins from methanol. The RadFrac model was used for the simulation of the separation tower. The HeatX model was used to simulate the heat exchanger. Methanol conversion rate was set as 99.9% and light olefins selection rate was 86%. The reaction temperature and pressure were 520 °C and 0.22 MPa, respectively. The light olefins were sent to the T101 to separate C₄₊ components after cooling down to 135 °C and compressing to 1.0 MPa. After the separation of C₄₊ components, then, it was sent to the T201 to remove CH₄ and H₂ at the condition of 3.0 MPa and −40 °C. A stream of propane, with the mass flow rate 30% of the light olefins, was also fed to the top tray of the T201 to

increase the temperature of the overhead condenser to −37 °C. Afterward, the light olefins entered the T202 to separate C₂ components from C₃ components at pressure of 2.5 MPa. The C₂ components were sent to the T301 to remove ethane at 1.5 MPa and produce ethylene with a molar purity of 99.97%. The C₃ components, after cooling down to 40 °C, were sent to the T302 to separate propane at 1.6 MPa and produce propylene with a molar purity of 99.98%.

2.3. RU units

The distribution is an important of criteria for evaluating the performance of a catalyst. The product distribution in MTO over two different regenerated catalysts was derived from the pilot experiments as shown in Table 2 [18]. The regeneration of spent SAPO-34 catalyst was carried out at the temperature of 680 °C, WHSV of 3 h^{−1}, catalyst loading of 5 g, flow rate of steam of 0.3 g · h^{−1}, and steam/coke ratio of 0.6. In the experiments the initial coke content of catalyst is 10%, and the regeneration time is in the range of 30–120 min. In this work, both air combustion and stream cracking

Table 2

Product distribution in MTO processes using different regeneration methods

Distribution/% (mass)	MTO-ACR	MTO-SR
CH ₄	0.76	1.34
C ₂ H ₄	16.92	21.80
C ₂ H ₆	0.32	0.49
C ₃ H ₆	16.53	14.07
C ₃ H ₈	1.12	0.71
C ₄	4.74	1.91
C ₅	1.85	0.73
C ₆	0.26	0.28
Coke	1.30	1.98
H ₂ O	55.40	55.69

regeneration methods were considered, in which the Rstoic model was implemented for simulating the regeneration process.

In a previous study by our same group, we used a MTO pilot plant, in which both fluidized bed reactor and regenerator, as well as the catalyst circulation lines, are developed for MTO process. We carried out the pilot plant experiments continuously for more than 105 h, and did not observe obvious degrading of the performance of SAPO-34 catalyst. Note that in this steady operation, the number of reaction-regeneration cycles would be significant, and typically results show that the light olefins selectivity can be 87% and methanol conversion more than 98% [18].

In the air combustion process, the catalyst activity is recovered by completely converting the deposited coke to flue gas with the composition shown in Table 3. For air combustion regeneration, the regeneration temperature is 650 °C, the pressure is about 0.12 MPa, and the conversion of coke is assumed to be 100%. Though in practical DMTO processes partial regeneration was widely used, here we considered completely regeneration in the model of MTO-ACR. For steam regeneration process, the activity of spent catalyst is partially recovered by steam cracking reaction after heat exchange, which occurs in the regenerator and produces CO, H₂, CH₄, and CO₂ as shown in Table 3. The partial regeneration occurs at temperature of about 680 °C, pressure of 0.2 MPa, and coke conversion of 30%. The conversion coke, which is mainly active species favoring light olefins selectivity, returning to the MTO reactor after heat exchange. Consider the production of light olefins from 1.8 million tons of methanol per year, the amount of coke is about 2.85 t·h⁻¹ and the deactivation rate of the catalyst would be about 28.5 t·h⁻¹.

Indeed, these two strategies have different conditions. For MTO with air combustion regeneration, the inactive coke species in spent catalyst will be burned off, forming carbon dioxide, and remove the coverage of active sites and blockage of nanopores inside zeolite catalyst. For MTO with steam regeneration, the inactive coke species in spent catalyst will be cracked into active coke species retained in the catalyst, with a small fraction (less than 30% of total coke) being transformed into syngas compounds as by-product. Thus, in MTO process with air combustion regeneration, the coke content can be directly related to the activity of catalyst, as shown by Li *et al.* [12] and Cordero-Lanzac *et al.* [13,39], since here the coke is essentially inactive polycyclic heavy aromatics. Basically, higher coke content suggests more coverage of active sites and more blockage of nanopores. In MTO process with steam regeneration, the coke content is no longer the direct indicator of the catalytic activity because during the regeneration the inactive coke species (polycyclic heavy aromatics) will be transformed to active coke species (low-cyclic aromatics).

The resource utilization of carbon dioxide has been paid much more attention [40–42]. However, we did not consider the conversion of carbon dioxide to methanol in current work. Carbon dioxide is generated in the regeneration with air combustion in MTO process. The flue gas from the regenerator contains a large amount of nitrogen and a little of carbon dioxide. Separating carbon dioxide from the nitrogen dominant flue gas poses a significant challenge due to its highly energy-intensive and high-cost

Table 3
Compositions of regeneration flue gas in MTO processes

Regeneration flue gas	MTO-ACR	MTO-SR
H ₂	0	6.88
O ₂	0.002	0
N ₂	76.71	0
CO	0	68.24
CH ₄	0	8.04
CO ₂	17.77	16.85
H ₂ O	5.33	0

Table 4
Simulation results for the key streams of MTO-ACR

Stream	Syngas	MeOH	Light olefins
Temperature/°C	25	54	520
Pressure/MPa	0.1	0.1	0.2
Mass fraction/%			
H ₂ O	0	0	55.4
CO	71.27	0	0
CO ₂	14.71	0	0
H ₂	13.10	0	0
CH ₃ OH	0	100	0.008
C ₂ H ₄ +C ₃ H ₆	0	0	33.45
Molar flow/kmol·h ⁻¹	22847.60	6830.40	9425.37
Mass flow/kg·h ⁻¹	242594	218861	218861

characteristic. In this sense, the reuse of carbon dioxide to synthesize methanol has not been considered in this manuscript. In fact, conversion of carbon dioxide to methanol also depends upon the availability and low-cost of hydrogen. According to Cordero-Lanzac *et al.* [40], the economic feasibility of carbon dioxide to methanol heavily relies on the volatility of H₂ and CO₂ prices, which are still expected to be reduced significantly.

3. Simulation Results

In our model, we assumed a MTO plant with capacity of 1.8 Mt·a⁻¹ methanol as feedstock and running time of 8000 h·a⁻¹. In addition, we considered the production chain from syngas via methanol to light olefins in the model because the syngas produced in MTO-SR is mixed with the feedstock syngas to form a closed loop. According to the results of simulations, the molar flows of the key streams can be calculated. Table 4 lists the simulation results for the key streams in MTO-ACR. Here syngas of 22847.6 kmol·h⁻¹ is fed to produce methanol of 6830.4 kmol·h⁻¹.

Simulation results for the key streams of MTO-SR are shown in Table 5. Clean syngas of 22847.6 kmol·h⁻¹ is used as the raw material and fed to the methanol synthesis unit. Subsequently, methanol of 6894.67 kmol·h⁻¹ is obtained. The amount of methanol produced in MTO-SR is a little bit more than that in MTO-ACR because of the recycled syngas from the steam regeneration of coke deposited in MTO catalyst.

Zhou *et al.* [18] conducted an experimental comparison on the lifetime of regenerated SAPO-34 catalyst in MTO reaction after steam regeneration and air combustion. They observed that the lifetime of the regenerated SAPO-34 catalyst by 120 min steam regeneration and 30 min air combustion was basically the same. Here, the lifetime is defined as the duration in which the methanol conversion is higher than 99%. Since the lifetime is almost the same, the reactor size would have minor difference for MTO process with steam regeneration and air combustion. Considering the investment in all the equipment, the minor distinction in reactor can be considered negligible. Therefore, the equipment investment is assumed to be the same under both regeneration conditions. Based on the above assumptions, the carbon utilization efficiency, energy efficiency, carbon dioxide emissions and economic performance under these two regeneration approaches were discussed in this work.

4. Performance Analysis

4.1. Carbon utilization efficiency

The carbon utilization efficiency is an important technical indicator, which is defined as the ratio between input molar flow rate

Table 5
Simulation results for the key streams of MTO-SR

Stream	Syngas	MeOH	Light olefins
Temperature/°C	25	54	520
Pressure/MPa	0.1	0.1	0.2
Mass fraction/%			
H ₂ O	0	4.79	55.69
CO	71.27	0	0
CO ₂	14.71	0	0
H ₂	13.10	0	0
CH ₃ OH	0	95.20	0
C ₂ H ₄ +C ₃ H ₆	0	0	35.87
Molar flow/kmol·h ⁻¹	22847.60	7241.81	10162.90
Mass flow/kg·h ⁻¹	242594	227174	227174

of carbon compounds and output molar flow rate of carbon compounds of target products. In this work, syngas is the input carbon compound while ethylene and propylene are outlet carbon compounds. The carbon utilization efficiency is thus defined as follows.

$$f = \frac{F_{\text{ethylene}} + F_{\text{propylene}}}{F_{\text{syngas}}} \times 100\% \quad (3)$$

where f is the carbon utilization efficiency, and F is the molar flow rate of carbon compounds.

For investigating the carbon utilization efficiency, carbon flow is shown in Fig. 4. For MTO-ACR, approximately 97.81% of the carbon in syngas can be converted to methanol in the MS unit. Following the MTO units, 74.74% of the total carbon is converted to light olefins. Approximately 1320.01 kmol·h⁻¹ ethylene and 859.72 kmol·h⁻¹ propylene are obtained. For MTO-SR, only 1.0% of carbon can be lost from MS unit, and 98.73% of carbon is fed into MTO unit, and ethylene of 1789.09 kmol·h⁻¹ and propylene of 769.80 kmol·h⁻¹ are obtained. Carbon efficiency of MTO-SR can be increased from 74.74% to 84.31% compared with that of MTO-ACR. Therefore, the MTO-SR can be used to improve the carbon utilization efficiency. Under this circumstance, the MTO-SR can save 285000 tons of coal compared MTO-ACR in the 0.6 Mt·a⁻¹ light olefins production plant.

4.2. Energy efficiency

The energy efficiency is used to analyze the technical performance of a designed process, and it can be determined as shown in Eq. (4) [43].

$$\eta = \frac{E_{\text{olefins}}}{E_{\text{syngas}} + E_{\text{util}}} \quad (4)$$

where η denotes the energy efficiency of the system under conditions of MTO-ACR or MTO-SR, E_{olefins} indicates the energy in the light olefin products, E_{syngas} represents the energy of syngas, and E_{util} represents the energy input of utilities (including steam and electricity). We calculated the energy of syngas and light olefins on the basis of their lower heating values [43]. The efficiency is measured based on the energy consumption in terms of syngas, ethylene, and propylene (10465, 59428.64, and 87592.05 kJ·m⁻³, respectively).

The energy efficiency for MTO-ACR and MTO-SR is shown in Fig. 5. For MTO-ACR, 6.99 m³ of syngas and 9.04 MJ of energy is consumed to produce 0.51 kg of ethylene and 0.49 kg of propylene. The energy efficiency for MTO-ACR is calculated to 57.22%. For MTO-SR, 6.20 m³ of syngas and 10.09 MJ of energy is consumed to produce 0.61 kg of ethylene and 0.39 kg of propylene. The energy

efficiency for MTO-SR is calculated to 63.57%. Therefore, the energy efficiency in MTO-SR is higher 6.35% than that of MTO-ACR, implying that MTO-SR has the advantage of higher energy efficiency.

4.3. Carbon dioxide emissions

The promotion of carbon utilization efficiency means the CO₂ emission reduction from the source of the system. Lifecycle carbon dioxide footprint analysis of MTO regeneration processes from syngas via methanol to light olefins as shown in Fig. 6. Besides the direct CO₂ emission, the indirect CO₂ emission associated with energy consumption also cannot be ignored [44]. Thus, the carbon dioxide emissions include direct and indirect emissions.

According to the life cycle analysis of carbon dioxide footprint, direct carbon dioxide emission mainly comes from the release gas and the regeneration unit, and indirect carbon dioxide emission mainly comes from the energy input in the process.

In MTO-ACR, the coke production is 1.3%, compared with 1.98% in MTO-SR. The coking rate in MTO-SR is slightly higher than that in MTO-ACR, because in MTO-SR there are more active species in SAPO-34 zeolites than that in MTO-ACR. These active species are mostly polymethyl benzene, which are more likely to generate coke in catalyst. However, in air combustion regeneration, all the carbon deposits were converted into carbon dioxide and water, while 30% of the coke was converted into carbon monoxide and hydrogen in steam treatment, and the rest into active species. The active species can be used to improve the conversion rate of light olefins and increase the selectivity of ethylene and propylene from 33.45% to 35.87%, thus increasing the yield of light olefins.

Based on life cycle carbon footprint analysis, the direct emissions for MTO-ACR and MTO-SR are 0.082, and 0.003 (t CO₂/t olefin), respectively. Therefore, the MTO-SR can be followed to significantly decrease the extent of green house gas (GHG) emissions [45]. The MTO-SR can be regarded as the near-zero carbon emission process in terms of direct emission. Considering the maximum heat recovery and the overall energy consumption, the total carbon dioxide emissions for MTO-ACR and MTO-SR are 1.09 and 0.83 t·t⁻¹, respectively. Taking the light olefins production plant with 600000 as an example, the annual carbon dioxide emissions of MTO-SR and MTO-ACR are approximately 546100 and 636400, respectively, as shown in Fig. 7. In comparison, steam regeneration process has the advantage of being environmentally friendly.

4.4. Economic performance

The economic performance of light olefins production for MTO-ACR and MTO-SR is studied [46,47]. For MTO-ACR, 6983.29 kmol·h⁻¹ of syngas and 662.69 GJ·h⁻¹ of energy are consumed to produce 2161.41 kmol·h⁻¹ of light olefins. For MTO-SR, 6983.29 kmol·h⁻¹ of syngas and 831.42 GJ·h⁻¹ of energy are required to produce 2535.61 kmol·h⁻¹ of light olefins. The cost and revenue for MTO-ACR and MTO-SR can be calculated out according to the prices of raw materials and products as shown in Table 6, and the net revenue of the system under conditions of MTO-ACR or MTO-SR is given in Eq. (5) [48,49].

$$\text{NR} = \text{PR} - \text{RMC} - \text{UC} \quad (5)$$

where NR denotes the net revenue of the system under conditions of MTO-ACR or MTO-SR, PR indicates the products revenue, RMC represents the raw materials cost, and UC represents the utilities cost.

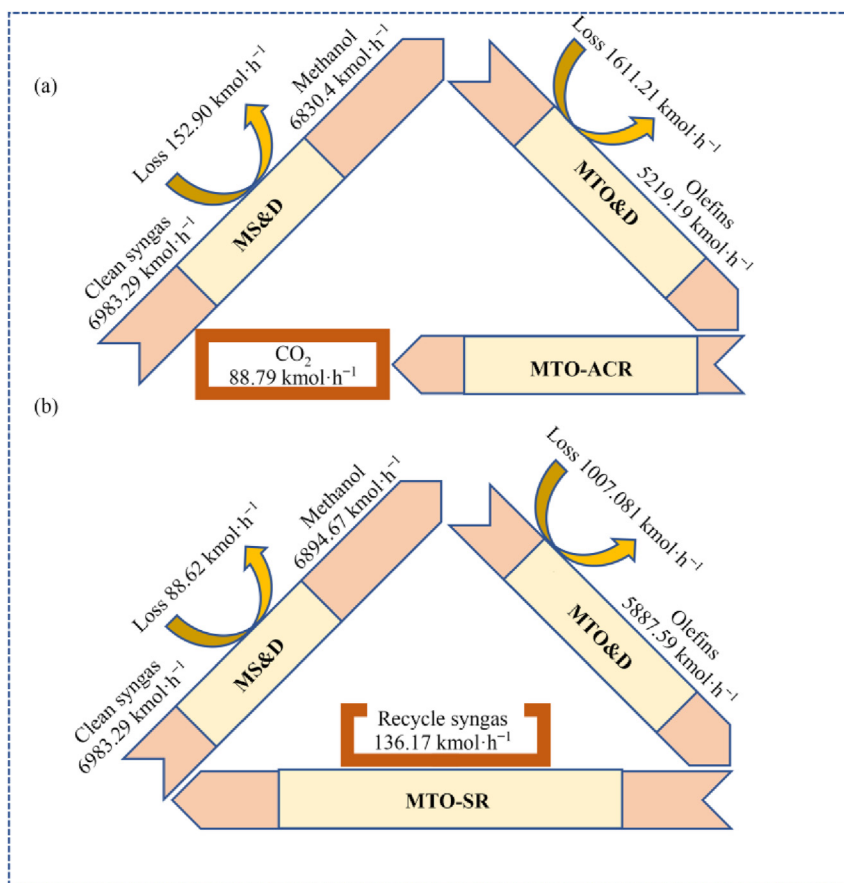


Fig. 4. Carbon flows for the (a) MTO-ACR and (b) MTO-SR.

It is assumed that the light olefins production plant with a yield of $0.6 \text{ Mt} \cdot \text{a}^{-1}$ and its total investment is 3.1 billion CNY, the lifespan of the plant is 20 years with a salvage value of 4% and the annual operation time is 8000 h. There were 255 operators, and the salary was 60000 CNY/operator/year [50,51]. Therefore, the total capital investment of MTO-ACR is the same as the MTO-SR, and the product cost of MTO-ACR and MTO-SR are shown in Fig. 8.

It is seen that the product cost the MTO-SR and MTO-ACR is 5003.89 and 5379.14 $\text{CNY} \cdot \text{t}^{-1}$ olefin, respectively. The raw material and the utilities cost of MTO-ACR and MTO-SR occupies 92.70% and 92.50% of the product cost, respectively, showing that the product

cost is mainly affected by raw material and utilities cost. Therefore, to reduce raw material and utilities cost, the proper system integration and optimization could be applied.

Compared with MTO-ACR, the production of light olefins in the MTO-SR is increased by $379.16 \text{ kmol} \cdot \text{h}^{-1}$ under the same amount of syngas feedstocks, implying that light olefins production of the MTO-SR is 17.39% higher than that MTO-ACR. However, higher reaction temperatures mean more energy consumption in the MTO-SR. The cost of utilities in MTO-SR is 1106.71 million $\text{CNY} \cdot \text{a}^{-1}$, and that of MTO-ACR is 957.39 million $\text{CNY} \cdot \text{a}^{-1}$. The cost of utilities in MTO-SR is higher by approximately 15.60% than that of MTO-ACR. However, the products revenue and net revenue for MTO-ACR and MTO-SR are 4867.40, 5683.21, 2734.07, and 2067.57 million $\text{CNY} \cdot \text{a}^{-1}$, respectively. The MTO-SR will get a lot more revenue on account of increased production of light olefins than that MTO-ACR as shown in Fig. 9.

The cost of syngas varies with the different feedstocks and process technologies as well as that its market supply and demand. The product costs of MTO-ACR and MTO-SR fluctuates with the price of syngas as shown in Fig. 10. When the price of syngas increases from 0.35 to $0.9 \text{ CNY} \cdot \text{m}^{-3}$, the product costs of MTO-ACR and MTO-SR would increase from 4395 to $8400.1 \text{ CNY} \cdot \text{t}^{-1}$ and 4169.64 to $7720.07 \text{ CNY} \cdot \text{t}^{-1}$, respectively, which means the product cost of MTO-ACR is slightly higher than that of MTO-SR.

Syngas as the initial material is used to simulate two regeneration paths in this study. Syngas can be obtained not only from coal gasification, but also from natural gas and biomass through a series of chemical reactions [52]. Compared to the traditional coal-to-olefin route, it has the advantage of low carbon emission to

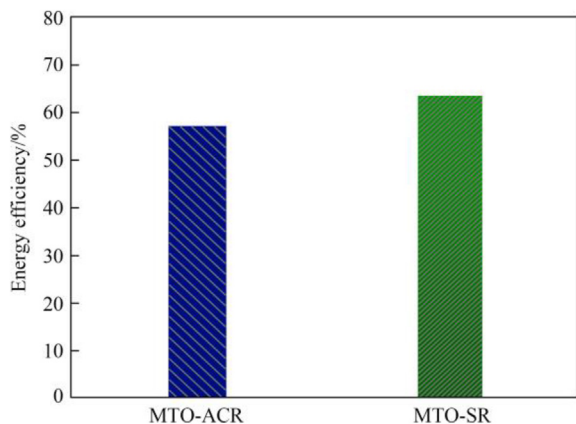


Fig. 5. Energy efficiency for the MTO-ACR and MTO-SR.

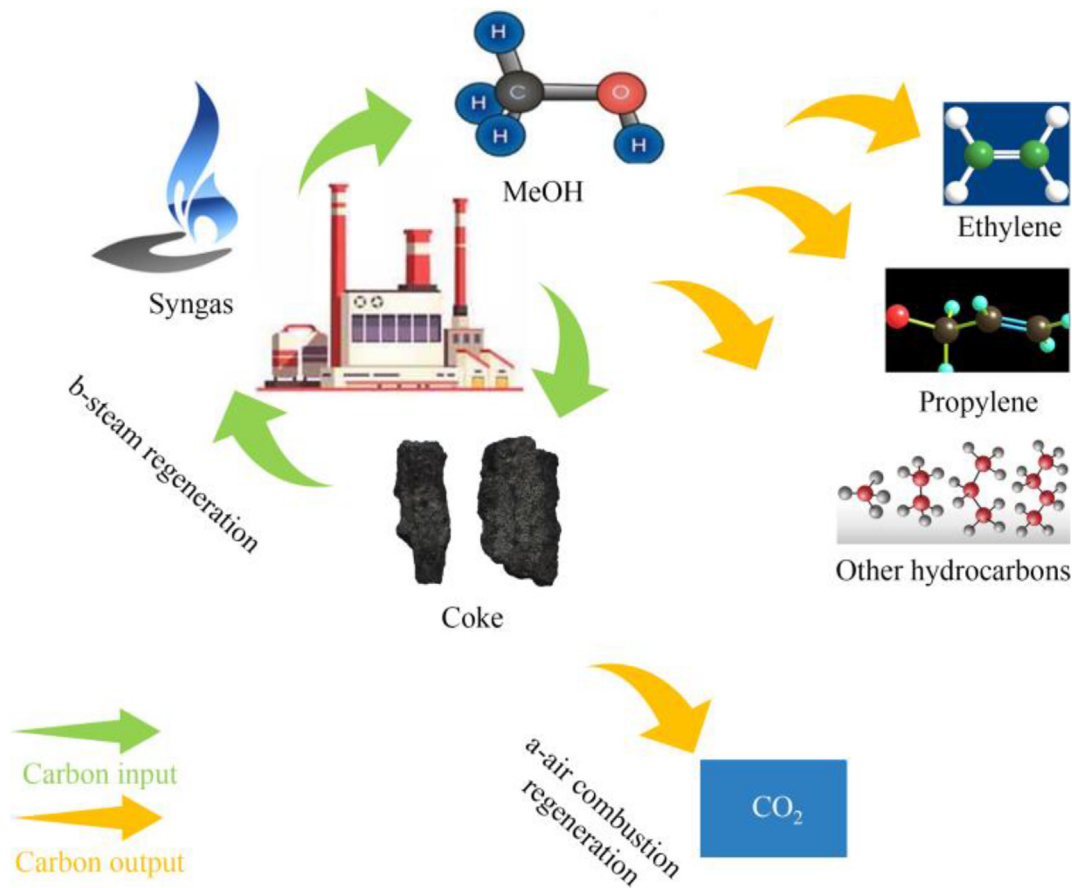


Fig. 6. Carbon footprint of MTO regeneration processes.

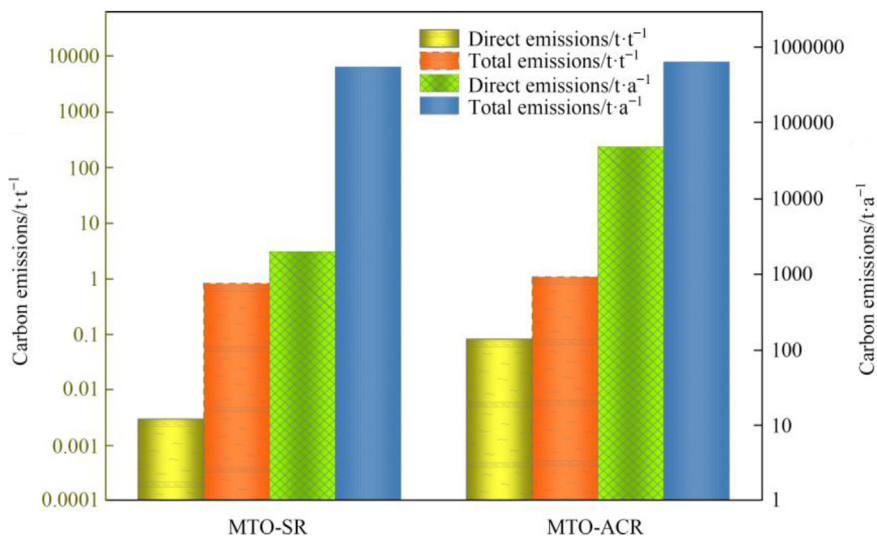


Fig. 7. Direct and total carbon emissions of MTO processes.

Table 6
Prices of raw materials and products

Items	Price	Items	Price	Items	Price
Ethane	3600	Propylene	7600	Steam	200
Ethylene	8800	Cooling water	3	Electricity	0.65
Propane	4200	Process water	15	Syngas	0.45

Note: Unit of the price of electricity is $\text{CNY} \cdot (\text{kW} \cdot \text{h})^{-1}$ and the unit of the price of syngas is $\text{CNY} \cdot \text{m}^{-3}$, the unit of other items is $\text{CNY} \cdot \text{t}^{-1}$.

produce the light olefins from natural gas and biomass [53,54]. However, due to the price of raw materials, the economic performance of coal to olefin is still superior to that of natural gas to olefin. When biomass becomes more readily available and the technologies of biomass to olefins are more proficient, biomass to olefin would be one of the most potential routes for light olefins production in the future [55].

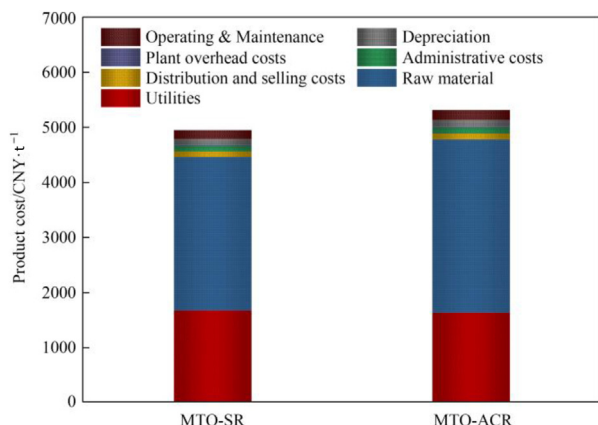


Fig. 8. Product costs of MTO-ACR and MTO-SR.

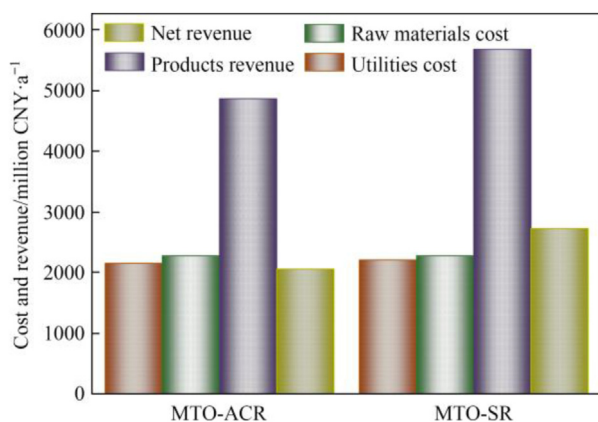


Fig. 9. Cost and revenue of MTO-ACR and MTO-SR.

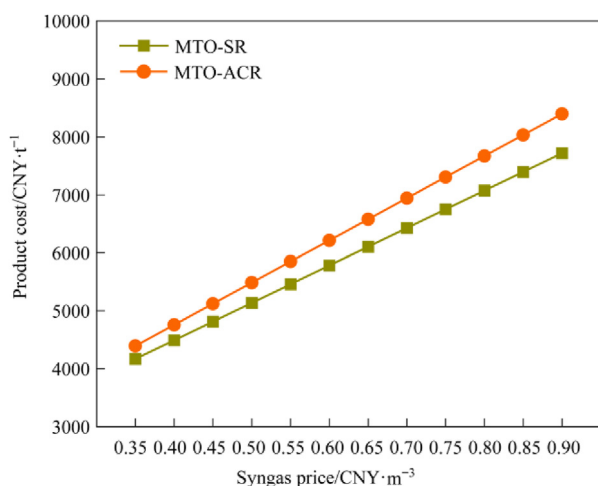


Fig. 10. Product costs of MTO-ACR and MTO-SR fluctuates with the price of syngas.

5. Conclusions

In this work, we compared the MTO-ACR and MTO-SR pathways based on the models and simulations implemented in the software Aspen Plus.

As can be found, MTO-SR manifests a higher carbon utilization efficiency compared with that MTO-ACR. The carbon utilization

efficiencies for MTO-ACR and that MTO-SR are 74.74% and 84.31%, respectively. The MTO-SR can be regarded as a near-zero carbon emission process with CO_2 emission of the process is reduced to $0.003 \text{ t} \cdot \text{t}^{-1}$. Moreover, the energy efficiency for MTO-SR is 6.35% higher than that MTO-ACR, implying that the MTO-SR is more energy efficient. Compared with that MTO-ACR, the production of light olefins in the MTO-SR is increased by $379.16 \text{ kmol} \cdot \text{h}^{-1}$ (or accounting for 17.39%) under the same amount of syngas feedstocks. The annual net revenue will increase by 556.68 million CNY for MTO-SR if the MTO-ACR is used as the baseline. It is shown that the MTO-SR can be considered as the most suitable promising option for catalyst regeneration in further MTO processes development from both the economic and environmental viewpoint.

Declaration of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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