



# Exergoenvironmental analysis of methanol production by steam reforming and autothermal reforming of natural gas<sup>★</sup>

Timo Blumberg<sup>a,\*</sup>, Young Duk Lee<sup>b</sup>, Tatiana Morosuk<sup>a</sup>, George Tsatsaronis<sup>a</sup>

<sup>a</sup> Institute for Energy Engineering, Technische Universität Berlin, Marchstr 18, 10587, Berlin, Germany

<sup>b</sup> Korea Institute of Machinery and Materials, 156 Gajeongbuk-ro, Yuseong-gu, Daejeon, 34103, South Korea

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## ABSTRACT

Methanol is one of the most important chemicals serving as a base for a range of synthetic fuels and variety of other chemical derivatives. Steam reforming and autothermal reforming of natural gas represent the major technologies used for syngas production in indirect low pressure methanol synthesis routes. Further process development is driven by technical and economic aspects, while environmental aspects often fade into the background. In this paper methanol production processes using steam reforming and autothermal reforming are investigated from the viewpoint of an exergoenvironmental analysis. The processes feature a coproduction of electricity for high efficiency. The pollutant formation within the chemical conversion units, particularly within the reformer and the furnace, reduces the environmental impact associated with the overall system. The environmental impact of generated methanol and electricity is calculated respectively as 156.4 mPt/kg and 98.2 mPt/MWh for the steam methane reforming process and has values of 134.0 mPt/kg and 71.3 mPt/MWh for the autothermal reforming process.

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## 1. Introduction

In the context of environment protection and global warming, the reduction of pollutants formation associated with the construction and operation of energy-intensive chemical plants is an ecological and economical issue. Therefore, the application of an adequate methodology for evaluation of the sources of pollutant formation is of relevance. Particularly for a bulk chemical and perspective energy carrier this can be very promising.

Methanol is one of the most important feedstock for the chemical and petrochemical industry with a forecasted demand of 117 million metric tons by 2020 [1]. The commercial applications range from further processing to bulk chemicals, for instance olefins and formaldehyde, to the production of synthetic fuels, such as DME (dimethyl ether) and MTBE (methyl-*tert*-butylether). The large significance has led to the term “methanol economy”, which proposes options to reduce pollution effects and thereby global

climatic changes [2]. A complete mitigation of pollutants in the production of methanol is aspired on a long term, while on a short term it is reasonable to expect that methanol is produced from fossil fuels like natural gas and coal by indirect synthesis routes via syngas production. Thus, for an estimation of the environmental impact of current industrial solutions, simulations need to be carried out in conjunction with adequate analysis tools.

A variety of methanol production processes are commercially available. They are primarily based on the chemical conversion of natural gas, being the main feedstock. Steam methane reforming (SMR), as the major technology, is an energy intensive process emitting a large amount of pollutants [3]. This technology is commercially used for methanol capacities of up to 2,500 mtpd, while above this production rate autothermal reforming (ATR) is the preferred technology due to better scalability. The methanol synthesis routes using SMR and ATR have been intensively investigated in the literature. In a previous study [3] a methanol process with SMR and carbon utilization through direct hydrogenation in the synthesis unit has been investigated from an exergetic point of view. The process only achieves a low exergetic efficiency of 37.7% while 0.42 tons of CO<sub>2</sub> per ton of methanol are integrated. In an older study conducted by Rosen et al. [4], the exergetic efficiency of a methanol process fed with syngas from SMR was calculated to be 39%. The utilization potential of CO<sub>2</sub> in the synthesis of methanol

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\* Corresponding author.

E-mail addresses: [blumberg@tu-berlin.de](mailto:blumberg@tu-berlin.de) (T. Blumberg), [ydllee@kimm.re.kr](mailto:ydllee@kimm.re.kr) (Y.D. Lee), [tetyana.morozuk@tu-berlin.de](mailto:tetyana.morozuk@tu-berlin.de) (T. Morosuk), [georgios.tsatsaronis@tu-berlin.de](mailto:georgios.tsatsaronis@tu-berlin.de) (G. Tsatsaronis).

Nomenclature			
$\dot{B}$	environmental impact rate associated with an exergy stream (Pts/s)	$L$	exergy loss
$b$	environmental impact per unit of exergy (Pts/J)	$k$	$k$ th component
$\dot{E}$	exergy flow rate (W)	$p$	exergy of product
$e$	specific exergy (J/kg)	tot	overall system
$f_b$	exergoenvironmental factor (%)	<i>Subscripts</i>	
$\dot{H}$	enthalpy flow rate (W)	CH	chemical
$h$	specific enthalpy (J/kg)	PH	physical
$j$	$j$ th stream	<i>Abbreviations</i>	
$\dot{m}$	mass flow rate (kg/s)	ATR	autothermal reforming
$p$	pressure (pa)	DME	dimethyl ether
$r_b$	relative environmental impact difference (%)	HHV	higher heating value
$y$	exergy destruction ratio (%)	HRSG	heat-recovery steam generator
$T$	temperature (K, °C)	LHHW	Langmuir-Hishlewood-Houston-Watson
<i>Greek symbols</i>		LHV	lower heating value
$\varepsilon$	exergetic efficiency (%)	LP	low pressure
$\eta$	energetic efficiency; isentropic efficiency of a compressor, pump, or expander (%)	MTBE	methyl- <i>tert</i> -butylether
<i>Superscripts</i>		Mtpd	metric tons per day
$D$	exergy destruction	NG	natural gas
$F$	exergy of fuel	NIST	national institute of standard and technology
		RKS	Redlich Kwong Soave
		SMR	steam methane reforming
		WGS	water-gas shift

has been profoundly investigated in recent study by Blumberg et al. [5]. The study shows that the integration of CO<sub>2</sub> is limited but nevertheless results in a large reduction of the required feedstock. Furthermore, an exergoeconomic analysis has been conducted for three processes based on SMR, ATR and two-step reforming [6]. The results showed that except for the SMR process, the analyzed plants can produce at a competitive market price. Comprehensive economic and exergy-based studies for a variety of synthesis routes based on SMR, ATR and dry methane reforming (DMR) have been carried out in Ref. [7]. The study shows that the goals of an increased sustainability and cost effectiveness are compatible. The study of Baltrusaitis et al. [8] investigated interesting combinations of different syngas generation technologies for direct preparation of the syngas composition to the downstream application. The authors of [9] performed a techno-economic analysis on a methanol-to-olefins process with very low CO<sub>2</sub> emissions based on autothermal reforming of natural gas. They figured out that the efficiency of the process highly depends on product variation (methanol, olefins and electricity).

Industrial methanol production is associated with a large amount of emissions and a depletion of natural resources, which can be assessed by life cycle assessment methods (LCA). Several studies analyzed the environmental impact of hydrogen production using a steam reforming process of natural gas. Spath et al. [10] carried out a comprehensive LCA and examined the net greenhouse gas emissions as well as other environmental consequences. Finally, the LCA is compared with other hydrogen production technologies. Boyano et al. [11] conducted a profound LCA on a SMR process estimating the environmental impact of each process unit based on the Eco Indicator 99. Yao et al. [12] analyzed the environmental emissions associated with different methanol production routes using natural gas and coal. The authors conclude that a renewable production of methanol should be the long-term goal to further promote the methanol economy. The environmental impact of a renewable production from CO<sub>2</sub> of biogas and hydrogen from

water electrolysis was investigated by Biernacki et al. [13]. Śliwińska et al. [14] conducted a LCA for a co-production system of methanol and electricity. The calculated greenhouse gas emissions of methanol from a reforming process of natural gas is 0.74 CO<sub>2</sub>-eq/kg. Further studies investigated the environmental impact of methanol production from different fuels, such as coke oven gas and sugarcane [14,15]. A study by Li et al. [16] shows, that the environmental burden of methanol production from natural gas has a 50–60% lower environmental impact compare to processes using coke oven gas or coal.

A variety of different approaches for combining exergetic and environmental analyses have been developed in the past. Among them are the cumulative exergy destruction by Szargut [17], extended exergy accounting by Sciubba [18], the exergoecological analysis by Valero [19], environomic analysis by Frangopoulos et al. [20] and the exergoenvironmental analysis by Meyer et al. [21]. In this study, the approach of the exergoenvironmental analysis [21] is applied. There are only a few publications dealing with exergoenvironmental analysis, some of which are given in the following. Lee et al. [22] applied an exergoenvironmental analysis to solid-oxide fuel cell hybrid power generation systems. Morosuk et al. [23] conducted an exergoenvironmental analysis and discussed the effect of the application of different environmental indicators on energy conversion systems at the example of a refrigeration system. Boyano et al. [11] conducted an exergoenvironmental analysis on a steam methane reforming process to assess the overall environmental impact for the production of hydrogen. The results show that the largest potential for lowering the environmental impact lies on the combustion reactor and the steam reformer.

The existing studies for methanol production processes using natural gas consider certain ecological aspects, such as the integration of CO<sub>2</sub> or the total emissions, without examining their formation and causes. Our study addresses this lack of information by investigating the environmental impact of individual process

units and the formation of emissions in conventional large-scale methanol production processes.

The two main synthesis routes for methanol production from natural gas, a SMR and ATR based route, are subject to an exergetic analysis and a life cycle assessment. Subsequently the results are combined in an exergoenvironmental analysis, which allows an explicit allocation of the environmental impact on several products and a determination of the impact of each process unit. The study makes the following novel contributions:

- Application of an exergoenvironmental analysis to complex chemical and thermal conversion systems such as a methanol reactor or distillation columns
- Estimation of the environmental impact of the main process units of conventional methanol synthesis routes
- Calculation of the environmental impact rate of a industrially produced methanol

## 2. Fundamentals of the synthesis route

For the recent decades, various concepts for methanol production by indirect synthesis routes via syngas production from natural gas have been proposed in the literature [6,23]. In general, the process units of each synthesis route consist of the following major sub-systems: a pretreatment unit for sulfur removal, a reforming unit for syngas production, a conditioning section for syngas adjustment, a synthesis unit for the methanol production from syngas (including a recycle loop of unconverted syngas), a purification section for refining the crude product, and a steam cycle for balancing the overall heat and electricity demand and supply of all the process units [3]. Among the enumerated sub-systems, the reforming and methanol synthesis unit are decisive in thermodynamic, economic and ecologic performance of a methanol plant. Therefore, the suitable selection of these process units is of particular importance.

### 2.1. Reforming technologies

Regarding the syngas production unit, the reforming technologies differ in construction, in supply of reforming agents and operation parameters. In this study, steam reforming and autothermal reforming are in the focus, since these technologies have been widely implemented on an industrial scale.

The syngas used in methanol synthesis theoretically should have a balanced composition of CO, CO<sub>2</sub>, and H<sub>2</sub>, which can be expressed by the stoichiometric S module defined in Eq. (1)

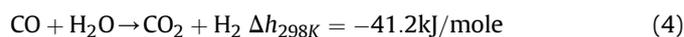
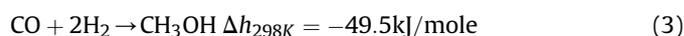
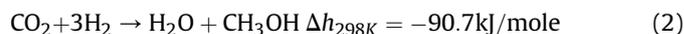
$$S = \frac{\dot{n}_{H_2} - \dot{n}_{CO_2}}{\dot{n}_{CO} + \dot{n}_{CO_2}} \quad (1)$$

Tubular fired steam reforming represents the predominating technology in methanol plants with capacities below 2,700 mtpd [24–26]. The endothermic reforming reactions take place over a nickel based catalyst at temperature between 800 and 1,000 °C under a pressure between 20 and 30 bar. Steam is also supplied as a reforming agent - the amount of steam supply is defined by the steam-to-carbon (S/C ratio), which typically has a value of 3.0 for a commercial scale reactor [23,27–29]. The composition and yield of the syngas are highly dependent on various operating parameters. A syngas from steam methane reforming contains a hydrogen surplus of around 40% resulting in a S module of close to three, deviating from the ideal value of two. The higher hydrogen contents decreases the methanol conversion rate, resulting in a large recycle flow back to the synthesis reactor. The large recycle flow

represents an energetic and economic burden to the synthesis unit. An addition of carbon dioxide downstream of the reformer would optimize the composition of syngas, allowing an improved value for the S module and thus an increasing conversion within the methanol synthesis reactor. Another possibility for an optimization of the syngas composition refers to the autothermal reforming technology. ATR is a combination of a steam reforming (SR) and a partial oxidation (POX)- both chemical reactions take place in one compact reactor. The ATR reactor vessel contains a combustion zone and a fixed catalyst bed within a refractory lined pressure shell. In ATR, oxygen or oxygen enriched air is deployed together with steam to partially oxidize the methane intake. Regarding the reaction parameters, the ATR is operated within a temperature range of 950 °C–1050 °C, a pressure range of 30–50 bar, a steam-to-carbon mole ratio (S/C ratio) of 0.5–1.5, and an oxygen-to-carbon mole ratio (O/C ratio) of 0.6–1.0 [23,29,30]. The syngas from an ATR reactor has a composition characterized by a S module value between 1.0 and 2.0. The large fraction of carbon monoxide results in a high reactivity of the syngas in the methanol reactor. The syngas leaving the reformer is of high temperature, thus requiring an intensive cooling before going next step.

### 2.2. Methanol synthesis

In the synthesis of methanol, carbon monoxide and carbon dioxide react with hydrogen according to the exothermic and non-equimolar reactions shown in Eqs. (2) and (3). Furthermore, CO and CO<sub>2</sub> are involved in the water gas shift reaction in Eq. (4), which strongly influences the reaction mechanism.



The synthesis of methanol is limited by the chemical equilibrium and favored at low pressure. However, in a commercial reactor, the temperature is controlled between 200 and 300 °C over a Ni/Zn/Al<sub>2</sub>O<sub>3</sub> catalyst at a pressure range of 50–100 bar. This operating condition results in a product yield of 5–15 mol-% [2,31,32]. Due to the low conversion rate, a large portion of the product gas is recycled to the inlet of the reactor. Even a small difference in conversion rate would result in large differences of the recirculation flow rate. As the recirculated inert components agglomerate in the recycle, a small part has to be purged from the synthesis loop. These features in conjunction with the catalyst performance and the metallurgical restrictions determine the design of a synthesis reactor and the configuration of synthesis loop.

The two major reactor technologies used in methanol synthesis refer to indirect-cooled isothermal reactors [2,28,33,34] and direct-cooled adiabatic quench reactors [36]. The synthesis concepts mainly differ in heat integration, make-up gas introduction, and removal of impurities.

In this study, an indirect-cooled isothermal shell and tube reactor is considered. The isothermal reactor is modelled based on [33] by referring to the Lurgi Steam Raising Reactor, one of the most widely employed commercial reactor technologies. More detailed information regarding the operating parameters and the reactor design is provided in the previous publications [5–7] of the authors.

### 3. System design and specifications

The indirect synthesis routes via syngas production by steam reforming and autothermal reforming of natural gas were simulated using the software Aspen Plus® [35]. The thermodynamic properties were calculated using the Redlich-Kwong-Soave equation of state. With respect to the isothermal methanol reactor, the kinetic inputs are taken from a study by vanden Bussche et al. [37], in which a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst is used for conversion of the feed. The kinetics is depicted by the Langmuir-Hishlewood-Houston-Watson (LHHW) model with implemented parameters from a study by Luyben et al. [38]. Power law kinetics based on [39] are used to model the SMR unit, while the combustion reactions in the ATR unit are assumed to achieve equilibrium. Simplified flow diagrams of the SMR and the ATR process are presented in Figs. 1 and 2. The corresponding stream data are provided in Tables 1 and 2.

Considering the SMR process, natural gas (stream 1) is supplied the process then compressed up to a pressure of 30 bar (by CM-01) to favor the reactions within the reformer. The gas is desulphurized in reactors R-01 and R-02, before the sweet gas enters an adiabatic pre-reformer, which serves for cracking higher hydrocarbons into methane. The product gas leaves the desulphurization unit with a temperature of 510 °C and a pressure of 27 bar. Subsequently, the effluent is blended with steam at a S/C-ratio of 3.5 before entering a regenerative heat exchanger. The methane is converted to syngas in a tubular fired steam reformer, where the heat for the endothermic steam reforming reaction is supplied by the combustion of 28.7 kg/s natural gas (stream 7) and tail gas (stream 13). The reformer comprises 3,500 tubes, each of them having a length of 12 m and a diameter of 0.1 m. A large mass flow of air (stream 8) is compressed to a pressure of 3.5 bar by steam turbine driven compressors CM-02. The process gas leaving the SMR unit has a temperature of 950 °C and a pressure of 20.5 bar.

The demand for combustion fuel and air are determined by the process heat demand of the reforming reactions. For high process efficiency, the low temperature heat of the combustion gases needs to be integrated into the other sub-systems. The hot gases leave the furnace with a temperature of 884 °C and are fed into a two-pressure level heat recovery steam generator (HRSG). Around 30% of the heat is integrated into the process by preheating the syngas in E-01 and by supplying steam with the R-02, R-03 and R-04. The remaining heat is recovered as steam on a high pressure level of 70 bar and a low-pressure level of 30 bar. The selection of the pressure levels is the result of an iterative optimization process for maximum power generation of the steam turbines T-01 and T-02.

The syngas from the reforming unit is compressed to the operating pressure of the synthesis unit by intercooled multistage compressors (CM-04 and CM-05). The syngas (stream 6), having a stoichiometric module of S equals 3, is blended with recycle streams of unconverted syngas, before entering the methanol reactor. Additionally, the syngas composition is adjusted by integration of a CO<sub>2</sub> stream for carbon utilization (stream 9). The integration of carbon species to the syngas stream leads to an increase in the methanol yield. However, a large amount of water is produced by the reverse water-gas shift (WGS) reaction, increasing the size and the energy demand of the distillation columns C-01 - C-03.

The syngas is preheated up to 250 °C by recovering thermal energy from the synthesis product before entering the synthesis reactor R-05. The preheating is required to achieve the minimum temperature of 220 °C to activate the reaction mechanism within the low pressure synthesis. The conversion rate of 6% results in large recycle flow rates of 390 kg/s and hence in large equipment dimensions of the reactor and the compressors. The reactor consists of 10,000 tubes, each of them having a diameter of 0.08 m and a length of 18 m [38]. The heat of the exothermic synthesis reaction is

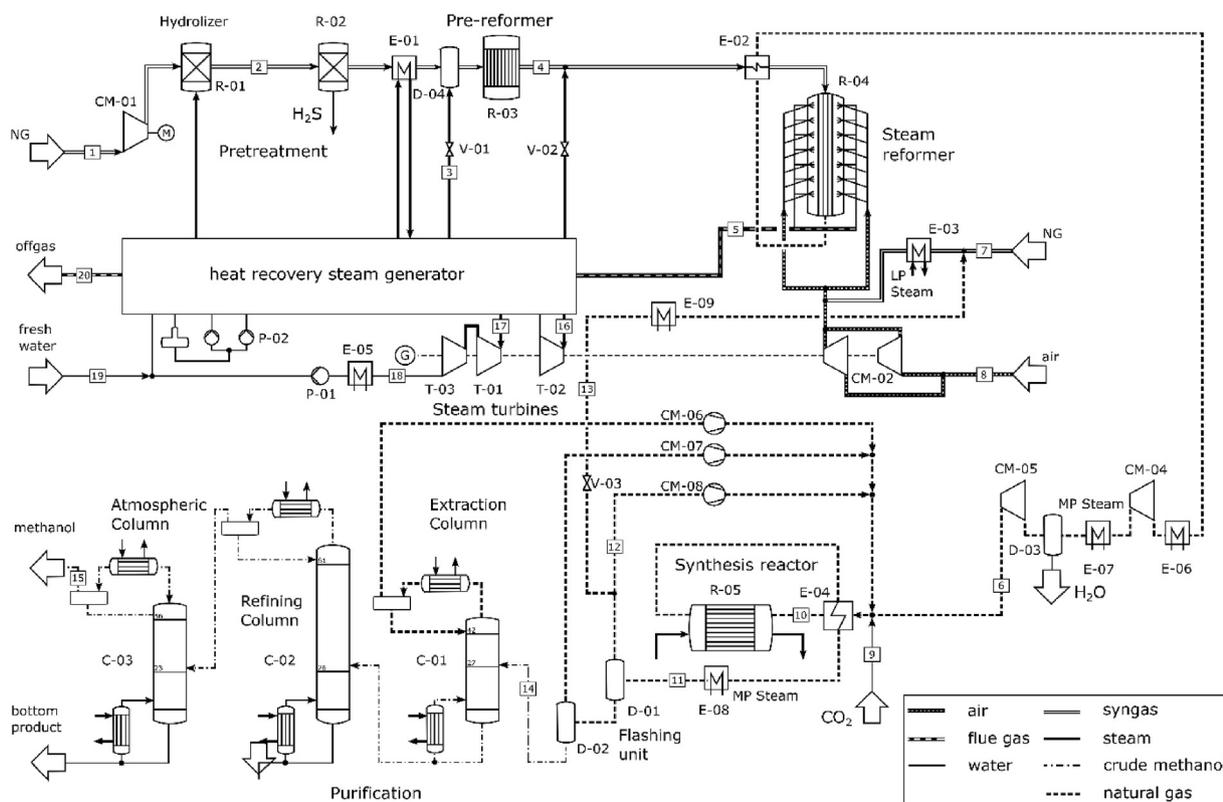


Fig. 1. Flowsheet of the SMR process [7].

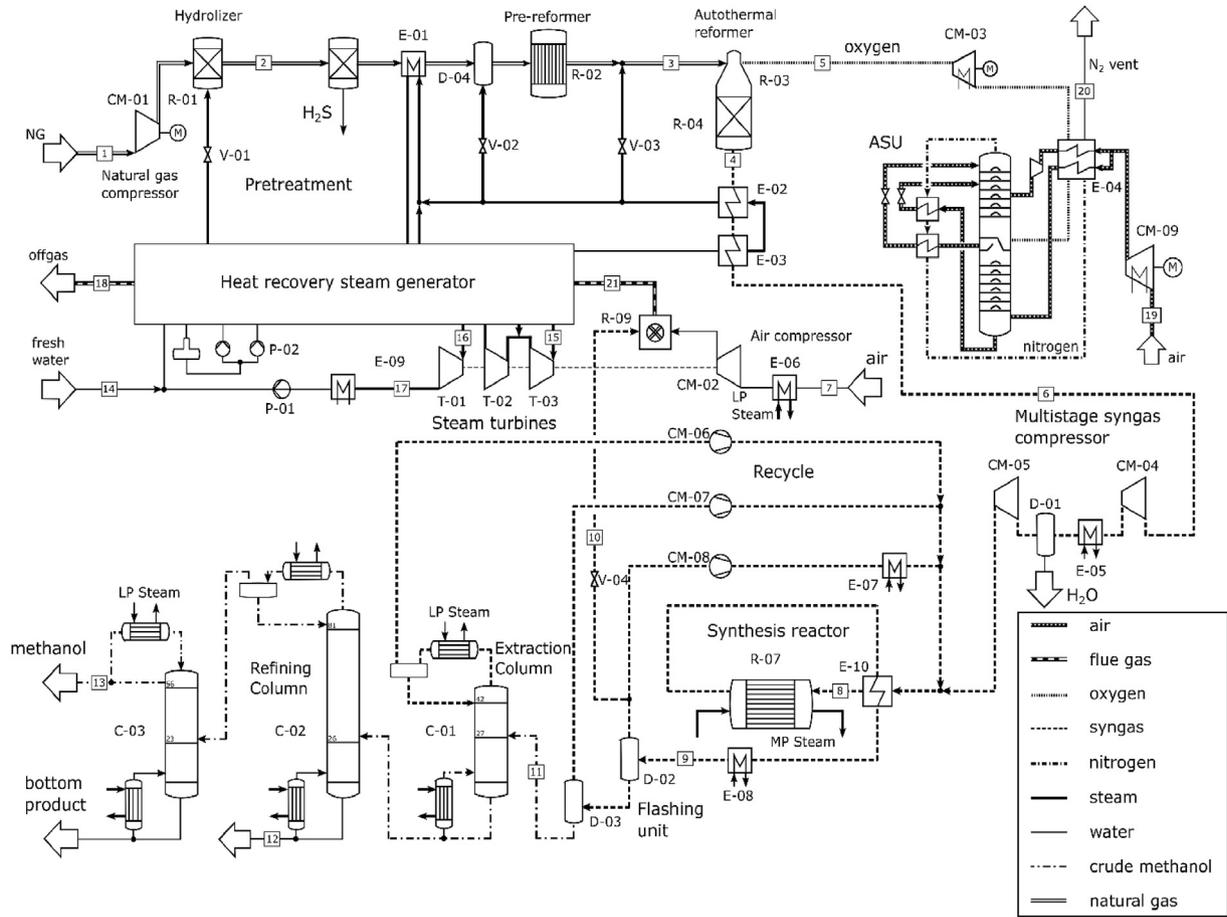


Fig. 2. Flowsheet of the ATR process [7].

Table 1  
Thermodynamic and environmental data of the streams in the SMR process.

Stream	Thermodynamic data						Exergoenvironmental analysis		
	$\dot{m}_j$ (kg/s)	$p_j$ (bar)	$T_j$ (°C)	$\dot{E}_j^{PH}$ (MW)	$\dot{E}_j^{CH}$ (MW)	$\dot{E}_j$ (MW)	$\dot{B}_j^{CH}$ (mPt/s)	$\dot{B}_j^{PH}$ (mPt/s)	$\dot{B}_j$ (mPt/s)
1	16.9	10.0	15.0	5.5	833.0	838.5	4,548.5	0.0	4,548.5
2	16.9	29.0	124.6	8.6	833.0	841.6	4,549.5	64.4	4,613.9
3	1.3	29.5	550.0	0.1	1.9	2.0	0.0	39.2	39.2
4	18.2	24.6	509.5	19.9	832.5	852.4	4,663.9	205.98	4,869.8
5	1,631.9	1.6	883.7	964.4	32.1	996.5	0.0	7,935.0	7,935.0
6	42.9	52.5	148.2	45.3	967.3	1,012.6	5,398.3	1,820.1	7,218.5
7	28.7	16.0	15.0	9.3	1,416.4	1,425.7	7,733.9	0.0	7,733.9
8	1,586.8	1.0	15.0	0.0	9.4	9.4	0.0	0.0	0.0
9	13.6	52.5	45.0	2.7	6.1	8.8	51.4	22.7	74.0
10	391.8	49.6	250.0	351.8	6,747.9	7,099.7	35,804.2	14,977.1	50,781.3
11	391.8	42.9	38.0	247.1	6,732.9	6,980.0	35,724.3	10,521.0	46,245.3
12	313.2	42.9	38.6	228.2	5,329.6	5,558.8	28,425.5	9,754.3	38,179.8
13	16.4	3.5	35.5	4.0	280.5	284.5	1,496.1	170.2	1,666.3
14	60.5	2.0	38.0	3.7	1,123.7	1,127.4	6,013.1	9.3	6,022.3
15	30.0	1.3	71.0	0.6	671.7	672.3	1,096.7	27.0	1,123.6
16	358.0	58.7	440.0	17.9	483.9	501.8	0.0	9,284.3	9,284.3
17	81.1	27.1	300.0	89.5	4.0	93.5	0.0	490.6	490.6
18	358.0	0.2	60.1	103.6	17.9	121.5	0.0	1,987.0	1,987.0
19	65.4	1.0	15.0	0.0	3.3	3.3	1.6	0.1	1.7
20	1,631.9	1.2	146.3	75.8	32.1	107.8	0.0	623.5	623.5

recovered as medium-pressure steam on the shell side. The heat is then supplied to the distillation columns to evaporate the bottom product at the reboilers. The synthesis product contains crude methanol, water and unconverted synthesis gas. Subsequently, the liquid phase and the vapor phase are separated in two flash drums

D-01 and D-02. The unconverted syngas is recycled to the reactor inlet using three centrifugal compressors (CM-06 – CM-08) to overcome the pressure drop within the synthesis unit. 5% of the mole flow rate of the fresh inlet gas is removed from the synthesis in order to avoid a build-up of inert components within the

**Table 2**  
Thermodynamic and environmental data of the streams in the ATR process.

Stream,j	Thermodynamic data						Exergoenvironmental analysis		
	$\dot{m}_j$	$P_j$	$T_j$	$\dot{E}_j^{\text{PH}}$	$\dot{E}_j^{\text{CH}}$	$\dot{E}_j$	$\dot{B}_j^{\text{CH}}$	$\dot{B}_j^{\text{PH}}$	$\dot{B}_j$
	(kg/s)	(bar)	(°C)	(MW)	(MW)	(MW)	(mPt/s)	(mPt/s)	(mPt/s)
1	22.8	10.0	15.0	7.4	1,124.6	1,131.9	6,140.4	0.0	6,140.4
2	22.8	39.8	155.3	13.1	1,124.6	1,137.7	6,140.7	65.6	6,206.3
3	36.7	34.8	558.5	46.9	1,124.9	1,171.8	6,146.0	4,928.2	11,074.2
4	60.2	33.3	922.6	121.0	975.4	1,096.4	6,167.2	7,513.2	13,680.4
5	23.6	34.8	277.0	8.0	2.5	10.5	0.0	84.5	84.5
6	60.2	25.2	157.0	43.3	975.4	1,018.7	6,167.2	2,687.7	8,854.9
7	418.3	1.0	15.0	0.0	2.5	2.5	0.0	0.0	0.0
8	207.2	50.7	250.0	176.3	3,587.0	3,763.3	22,791.7	8,392.6	31,184.3
9	207.2	44.8	38.0	116.9	3,573.5	3,690.4	22,706.3	5,564.8	28,271.1
10	18.9	4.0	38.2	12.8	313.5	326.3	1,999.0	606.0	2,605.0
11	33.8	2.0	38.0	0.1	711.3	711.4	4,549.0	5.6	4,554.6
12	0.9	2.8	133.0	0.09	0.04	0.13	0.2	3.9	4.1
13	28.4	1.3	70.9	0.5	637.2	637.7	1,572.6	22.3	1,594.9
14	13.9	1.0	15.0	0.0	0.7	0.7	0.4	0.0	0.4
15	61.3	175.3	600.0	101.8	3.1	104.9	0.0	1,020.4	1,020.4
16	130.2	15.0	218.3	124.6	6.5	131.1	0.0	1,011.1	1,011.1
17	130.2	0.4	76.0	48.2	6.5	54.7	0.0	391.1	391.1
18	437.2	1.9	110.0	7.1	32.6	39.7	0.0	184.5	184.5
19	101.6	1.0	15.0	0.0	0.6	0.6	0.0	0.0	0.0
20	76.9	3.3	17.9	2.0	7.7	9.7	0.0	112.6	112.6
21	437.2	2.5	817.1	7.1	244.7	251.8	0.0	1,383.7	1,383.7

synthesis loop. The tail gas (stream 13) is used as a combustion fuel in the reforming unit, contributing to the reduction of the natural gas use. Having 73 mol-% methanol purity, the crude product still contains a considerable amount of water and other impurities. In the extraction column C-01, the light ends, including hydrogen, methane, carbon monoxide and nitrogen, are removed from the crude product and recycled to the reactor inlet. The bottom product is further purified in a refining column C-02 and an atmospheric column C-03, which separates water from the methanol.

The autothermal reforming process, shown in Fig. 2, generally features a less complex configuration, but requires an air separation unit (ASU) as an additional subsystem. Compared to the first process (SMR process), the design of the heat integration system is different, since the reforming unit represents a heat source instead of a heat sink. Consequently, the process heat can only be generated by burning the recycled tail gas (stream 13).

A natural gas flow of 22.8 kg/s is compressed up to a pressure of 40 bar to allow a high methane conversion within the combustion and catalytic zone of the ATR (R-03 and R-04). The operating parameters of the ATR were selected based on the results of sensitivity analyses reported by authors [7]. Oxygen and steam are supplied to the combustion zone (R-03) and the catalytic zone (R-04) at a O/C and S/C-ratio of 0.55 and 0.6, respectively. The oxygen is provided with a purity of 95 mol-% by an air separation unit (ASU).

The discharge from the reformer is cooled in E-02 and E-03 before being compressed in CM-04 and CM-05 up to the operating pressure of the synthesis reactor. Thanks to the elevated reforming pressure, the energy demand for the syngas compression unit is low. The total circulating mass flow (stream 9) is determined only at 207.2 kg/s primarily due to the high conversion rate in the synthesis reactor (R-03) and the purge ratio of 11%.

Despite of the moderate concentration of water in the crude product (8 mol-%), a three column distillation is required to produce AA grade methanol. In comparison to the SMR process having a water content of 25% in the crude product, the heat duty of the reboiler heat exchangers is low.

The process heat for steam production is primarily recovered from the syngas flow exiting R-03 (within the coolers E-02, E-03, E-05) and by combustion of the purge gas from the synthesis unit in

R-09. Heat is recovered in the form of steam at two pressure levels (80 bar and 200 bar), generating electricity within a set of steam turbines (T-01 – T-03). The low-pressure ASU using an intercooled multistage compressor can not be integrated into heat recovery system.

#### 4. Methodology

An exergoenvironmental analysis is a powerful tool to assess an energy- or chemical-conversion system from an environmental point of view. The analysis combines a conventional exergy analysis and life cycle assessment (LCA). An exergy analysis constitutes a convenient method to assess the quality of resources and to identify and quantify the thermodynamic inefficiencies within energy-intensive chemical processes. An LCA provides information on the environmental impact of a stream, a component, and an overall system. Using an exergoenvironmental analysis, the environmental impacts obtained from the LCA are appropriately assigned to the exergy streams, identifying the components with highest environmental impact and the options for possible improvements [10]. The methodology comprises the following steps: in the first step an exergy analysis is carried out as well as LCA is conducted in order to calculate the environmental impact of all input streams. In the second step, the environmental impacts are assigned to all exergy streams within the system. Subsequently, exergoenvironmental variables are calculated for each component and an exergoenvironmental evaluation will be made using the information obtained above.

##### 4.1. Exergy analysis

Exergy analysis represents a well-known methodology for identifying the locations, magnitude, and the sources of thermodynamic inefficiencies in an energy-conversion system [40]. The exergy analysis has been widely applied to various analyses of energy system and has been proven to be advantageous in a more effective use of energy resources [3–7].

The exergy rate  $\dot{E}_j = \dot{m}_j e_j$  of the  $j$  th stream of matter includes the sum of the chemical and physical exergy for each material

stream. The effects of kinetic and potential exergies are neglected

$$\dot{E}_j = \dot{E}_j^{\text{CH}} + \dot{E}_j^{\text{PH}} = \dot{m}_j (e_j^{\text{CH}} + e_j^{\text{PH}}) \quad (5)$$

The model of Szargut [41] is chosen for the specific standard chemical exergies. The ambient conditions are assumed to be  $T_0 = 15^\circ\text{C}$  and  $p_0 = 1.013$  bar.

The exergy balance for the overall system can be written using the approach “exergy of fuel/exergy of product” [39,41,42].

$$\dot{E}_{\text{F,tot}} = \dot{E}_{\text{P,tot}} + \sum_k \dot{E}_{\text{D},k} + \dot{E}_{\text{L,tot}} \quad (6)$$

With reference to the analyzed systems shown in Figs. 1 and 2, the exergy losses  $\dot{E}_{\text{L}}$  are mainly related to the offgas leaving the heat recovery steam generator and the bottom product from the distillation columns. The exergy of product of the overall system  $\dot{E}_{\text{P,tot}}$  comprises the product methanol ( $\dot{E}_{\text{P,Meoh}}$ ) and the net electricity ( $\dot{W}_{\text{NET}}$ ) that is generated in the steam cycle. Natural gas as a combustion fuel for process heat generation within the reforming unit and as a feedstock for syngas production represent the exergy of fuel  $\dot{E}_{\text{F,tot}}$  of the overall system (termed as  $\dot{E}_{\text{CH}_4,\text{Syngas}}$  and  $\dot{E}_{\text{CH}_4,\text{Fuel}}$ ). The exergy destruction rate for the  $k$ th component ( $\dot{E}_{\text{D},k}$ ) can be calculated from the exergy balance

$$\dot{E}_{\text{D},k} = \dot{E}_{\text{F},k} - \dot{E}_{\text{P},k} \quad (7)$$

The definitions of the exergy of product ( $\dot{E}_{\text{P},k}$ ) and the exergy of fuel ( $\dot{E}_{\text{F},k}$ ) for selected components are listed in Table 3. The ratio of the exergy destruction rate of the  $k$ th component and the exergy rate of fuel of the overall system  $\dot{E}_{\text{F,tot}}$  is referred to as exergy destruction ratio  $y_{\text{D},k}$ , while the variable  $y_{\text{D},k}^*$  is calculated as the ratio of  $\dot{E}_{\text{D},k}$  and the entire exergy destruction rate within the overall system  $\dot{E}_{\text{D,tot}}$ . The exergetic efficiency  $\varepsilon$  is the ratio of the exergy of product to the exergy of fuel. For the overall system

$$\varepsilon_{\text{tot}} = \frac{\dot{E}_{\text{P,tot}}}{\dot{E}_{\text{F,tot}}} = \frac{\dot{W}_{\text{NET}} + \dot{E}_{\text{Meoh}}}{\dot{E}_{\text{CH}_4,\text{Syngas}} + \dot{E}_{\text{CH}_4,\text{Fuel}}} \quad (8)$$

#### 4.2. Life cycle assessment

To analyze the environmental characteristics, a life cycle assessment (LCA) for each component within the process and for each input stream entering the overall system is required. LCA is an established and internationally standardized method for the assessment of environmental aspects over a entire life cycle of services and products [43]. Application of an LCA to a chemical or energy conversion system includes an inventory analysis, identifying and quantifying the consumption and release of materials and energy flows. The laws of conservation of mass and energy form the base for the inventories calculation of the system being analyzed. The quantitative environmental impact of processes and products is assessed by using a specific indicator.

A variety of indicators have been developed, such as the Eco-Indicator 95 [44], the Eco-Indicator 99 [45], EDIP 2003 [46] and Ecoinvent [47]. However, only a limited number of indicators can be applied to energy conversion systems, due to the availability of adequate data. In this study, the Eco-Indicator 99 based life cycle impact assessment method [45] is applied, since it considers different environmental aspects and uses average European data.

A lifetime of 20 years and 8000 h of annual operating time are assumed. The consumption of natural gas, process water, cooling water, and carbon dioxide is considered for the calculation of the environmental impact of components and streams. The

environmental impact per unit of exergy for process water and cooling water after decarbonisation is  $b_{\text{Process water}} = 0.026$  mPt/kg and  $b_{\text{Cooling water}} = 0.0026$  mPt/kg [11]. The values of the environmental impact for various emissions have been obtained from Refs. [11,21] and are summarized in Table 4.

#### 4.3. Exergoenvironmental evaluation

The exergoenvironmental analysis was proposed as a new approach by Meyer et al. [21]. The purpose of an exergoenvironmental analysis is to identify the environmental impact of each component and stream. An assignment of the results of an environmental analysis to exergy streams is conducted in analogy to the assignment of costs to exergy streams in exergoeconomics. The environmental impact rate  $\dot{B}_j$  is expressed in Eco-indicator points per unit of time (Pts/s or mPts/s).

$$\dot{B}_j = b_j \dot{E}_j \quad (8)$$

where  $b_j$  is the specific environmental impact per unit of exergy of the  $j$ th stream (Pts/MJ or mPts/MJ). The values of  $b_j$  for different gaseous components are provided in Table 4. To increase the accuracy of the analysis, it is useful to distinguish between the environmental impact associated with the chemical and the physical exergy of a material stream.

$$\dot{B}_j = \dot{B}_j^{\text{CH}} + \dot{B}_j^{\text{PH}} = b_j^{\text{CH}} \dot{E}_j^{\text{CH}} + b_j^{\text{PH}} \dot{E}_j^{\text{PH}} = b_j \dot{E}_j \quad (9)$$

An environmental impact balance for the  $k$ th system component can be written according to Ref. [21] as

$$\dot{B}_{\text{P},k} = \dot{B}_{\text{F},k} + \dot{Y}_k \quad (10a)$$

$$b_{\text{P},k} \dot{E}_{\text{P},k} = b_{\text{F},k} \dot{E}_{\text{F},k} + \dot{Y}_k \quad (10b)$$

where  $\dot{B}_{\text{P},k}$  and  $\dot{B}_{\text{F},k}$  refer to the environmental impact rates of the product and fuel, whereas  $b_{\text{P},k}$  and  $b_{\text{F},k}$  represent the corresponding environmental impact per unit of exergy product and fuel, respectively. The variable  $\dot{Y}_k$  refers to the component-related environmental impact associated with the life cycle of the  $k$ th component, including the three life cycle phases of construction (manufacturing, transport and installation)  $\dot{Y}_k^{\text{CO}}$ , operation and maintenance  $\dot{Y}_k^{\text{OM}}$ , and disposal and dismantling  $\dot{Y}_k^{\text{DI}}$ , and is calculated according to (11)

$$\dot{Y}_k = \dot{Y}_k^{\text{CO}} + \dot{Y}_k^{\text{OM}} + \dot{Y}_k^{\text{DI}} \quad (11)$$

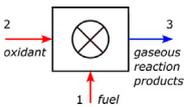
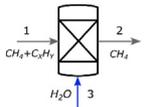
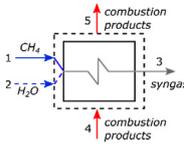
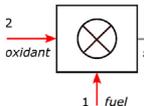
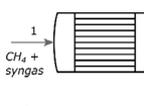
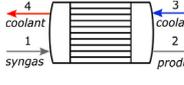
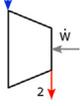
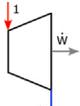
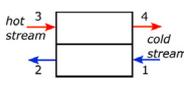
However, in this study, the environmental impact associated with the system components is neglected, as other studies showed, that the contribution of the component-related environmental impact of  $\dot{Y}_k$  to the total environmental impact of a component is very small. Another variable  $\dot{B}_k^{\text{PF}}$  should be introduced to account for the pollutant formation within the  $k$ th component. This term should not be calculated if no pollutants are formed, for instance for systems without a chemical reaction. For components incorporating chemical reactions, the value of  $\dot{B}_k^{\text{PF}}$  can be calculated as

$$\dot{B}_k^{\text{PF}} = \sum_i b_i (\dot{m}_{i,\text{out}} - \dot{m}_{i,\text{in}}) \quad (12)$$

$$\dot{B}_{\text{P},k} = \dot{B}_{\text{F},k} + \dot{Y}_k + \dot{B}_k^{\text{PF}} \quad (13)$$

Here, only pollutant substances which finally are emitted to the

**Table 3**  
Definition of the exergy of product and the exergy of fuel for the main components.

Component/ Assumption	$\dot{E}_{F,k}$	$\dot{E}_{P,k}$	$\dot{B}_{F,k}$	$\dot{B}_{P,k}$
Furnace* 	$\dot{E}_1^{CH} + \dot{E}_2^{CH} - \dot{E}_3^{CH}$	$\dot{E}_3^{PH} - \dot{E}_1^{PH} - \dot{E}_2^{PH}$	$\dot{B}_1^{CH} + \dot{B}_2^{CH} - \dot{B}_3^{CH}$	$\dot{B}_3^{PH} - \dot{B}_1^{PH} - \dot{B}_2^{PH}$
Pre-reformer 	$(\dot{E}_1^{CH} - \dot{E}_1^{CH,CH_4} - \dot{E}_1^{CH,CO} + \dot{E}_1^{PH} + (\dot{E}_2^{CH,CH_4} + \dot{E}_2^{CH,CO}) - \dot{E}_3^{CH} - \dot{E}_2^{PH} - (\dot{E}_2^{CH} - \dot{E}_2^{CH,CH_4} - \dot{E}_2^{CH,CO}) - \dot{E}_{12}^{CH,CO})$	$(\dot{E}_3^{CH,CH_4} + \dot{E}_1^{CH,CO})$	$(\dot{B}_1^{CH} - \dot{B}_1^{CH,CH_4} - \dot{B}_1^{CH,CO}) + \dot{B}_1^{PH} + (\dot{B}_2^{CH,CH_4} + \dot{B}_2^{CH,CO}) - (\dot{B}_1^{CH,CH_4} + \dot{B}_1^{CH,CO})$	$\dot{B}_3^{PH} - \dot{B}_2^{PH} - (\dot{B}_2^{CH} - \dot{B}_2^{CH,CH_4} - \dot{B}_1^{CH,CO}) - \dot{B}_{12}^{CH,CO}$
Steam reformer* 	$(\dot{E}_1^{CH} - (\dot{E}_1^{CH,H_2} - \dot{E}_1^{CH,CO} - \dot{E}_1^{CH,CO_2}) - (\dot{E}_3^{CH} - \dot{E}_3^{CH,H_2} - \dot{E}_3^{CH,CO} - \dot{E}_3^{CH,CO_2}) + \dot{E}_4^{PH} - \dot{E}_5^{PH})$	$(\dot{E}_3^{PH} - \dot{E}_1^{PH} - \dot{E}_2^{PH} + \dot{E}_3^{CH,CO} + \dot{E}_3^{CH,CO_2} + \dot{E}_3^{CH,H_2} - \dot{E}_1^{CH,CO} - \dot{E}_1^{CH,CO_2} - \dot{E}_1^{CH,H_2})$	$(\dot{B}_1^{CH} - \dot{B}_1^{CH,H_2} - \dot{B}_1^{CH,CO} - \dot{B}_1^{CH,CO_2}) - (\dot{B}_3^{CH} - \dot{B}_3^{CH,H_2} - \dot{B}_3^{CH,CO} - \dot{B}_3^{CH,CO_2}) + \dot{B}_4^{PH} - \dot{B}_5^{PH}$	$\dot{B}_3^{PH} - \dot{B}_1^{PH} - \dot{B}_2^{PH} + \dot{B}_3^{CH,H_2} + \dot{B}_3^{CH,CO} + \dot{B}_3^{CH,CO_2} - \dot{B}_1^{CH,H_2} - \dot{B}_1^{CH,CO} - \dot{B}_1^{CH,CO_2} -$
Autothermal reformer combustion zone 	$(\dot{E}_1^{CH} - \dot{E}_1^{CH,CO} - \dot{E}_1^{CH,CO_2} - \dot{E}_1^{CH,H_2}) - \dot{E}_2^{CH} - (\dot{E}_3^{CH} - \dot{E}_3^{CH,CO} - \dot{E}_3^{CH,CO_2} - \dot{E}_3^{CH,H_2})$	$(\dot{E}_3^{PH} - \dot{E}_1^{PH} - \dot{E}_2^{PH} + \dot{E}_3^{CH,CO} + \dot{E}_3^{CH,CO_2} + \dot{E}_3^{CH,H_2} - \dot{E}_1^{CH,CO} - \dot{E}_1^{CH,CO_2} - \dot{E}_1^{CH,H_2})$	$(\dot{B}_1^{CH} - \dot{B}_1^{CH,CO} - \dot{B}_1^{CH,CO_2} - \dot{B}_1^{CH,H_2}) - \dot{B}_2^{CH} - (\dot{B}_3^{CH} - \dot{B}_3^{CH,CO} - \dot{B}_3^{CH,CO_2} + \dot{B}_3^{CH,H_2})$	$\dot{B}_3^{PH} - \dot{B}_1^{PH} - \dot{B}_2^{PH} + \dot{B}_3^{CH,CO} + \dot{B}_3^{CH,CO_2} + \dot{B}_3^{CH,H_2} - \dot{B}_1^{CH,CO} - \dot{B}_1^{CH,CO_2} - \dot{B}_1^{CH,H_2}$
Autothermal reformer catalytic zone 	$(\dot{E}_1^{CH} - \dot{E}_1^{CH,CO} - \dot{E}_1^{CH,H_2} - \dot{E}_1^{CH,CO_2}) - (\dot{E}_2^{CH} - \dot{E}_2^{CH,CO} - \dot{E}_2^{CH,CO_2} - \dot{E}_2^{CH,H_2})$	$(\dot{E}_2^{CH,CO} + \dot{E}_2^{CH,H_2} + \dot{E}_2^{CH,CO_2}) - (\dot{E}_1^{CH,CO} + \dot{E}_1^{CH,H_2} + \dot{E}_1^{CH,CO_2}) - \dot{B}_2^{CH,CO_2}$	$(\dot{B}_1^{CH} - \dot{B}_1^{CH,CO} - \dot{B}_1^{CH,H_2} - \dot{B}_1^{CH,CO_2}) - (\dot{B}_2^{CH} - \dot{B}_2^{CH,CO} - \dot{B}_2^{CH,H_2} - \dot{B}_2^{CH,CO_2})$	$(\dot{B}_2^{CH,CO} + \dot{B}_2^{CH,H_2} + \dot{B}_2^{CH,CO_2}) - (\dot{B}_1^{CH,CO} + \dot{B}_1^{CH,H_2} + \dot{B}_1^{CH,CO_2})$
Synthesis reactor* $T_2 \geq T_1$ 	$(\dot{E}_1^{CH} - \dot{E}_1^{CH,CH_3OH}) - (\dot{E}_2^{CH} - \dot{E}_2^{CH,CH_3OH})$	$(\dot{E}_2^{PH} - \dot{E}_1^{PH}) + (\dot{E}_2^{CH,CH_3OH} - \dot{E}_1^{CH,CH_3OH}) + (\dot{E}_4^{PH} - \dot{E}_3^{PH})$	$(\dot{B}_1^{CH} - \dot{B}_1^{CH,CH_3OH}) - \dot{B}_2^{CH} - \dot{B}_2^{CH,CH_3OH}$	$(\dot{B}_2^{PH} - \dot{B}_1^{PH}) + (\dot{B}_2^{CH,CH_3OH} - \dot{B}_1^{CH,CH_3OH}) + (\dot{B}_4^{PH} - \dot{B}_3^{PH})$
Compressor* $T_1 \geq T_0$ 	$\dot{W}_{CM}$	$\dot{E}_2 - \dot{E}_1$	$\dot{W}_{CM} * b_{el}$	$\dot{B}_2 - \dot{B}_1$
Expander* $T_2 \geq T_0$ 	$\dot{E}_1 - \dot{E}_2$	$\dot{W}_{EXP}$	$\dot{B}_1 - \dot{B}_2$	$\dot{W}_{EXP} * b_{el}$
Heat Exchanger* $T_1 \geq T_0$ 	$\dot{E}_3^{PH} + \dot{E}_3^{CH} - \dot{E}_4^{PH} - \dot{E}_4^{CH}$	$\dot{E}_2^{PH} + \dot{E}_2^{CH} - \dot{E}_1^{PH} - \dot{E}_1^{CH}$	$\dot{B}_3^{PH} + \dot{B}_3^{CH} - \dot{B}_4^{PH} - \dot{B}_4^{CH}$	$\dot{B}_2^{PH} + \dot{B}_2^{CH} - \dot{B}_1^{PH} - \dot{B}_1^{CH}$

environment have been considered, e.g.  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}_x$  and  $\text{SO}_x$  [21]. The value of  $\dot{B}_k^{\text{PF}}$  is positive if the mass flow rate of a pollutant increases within the  $k$ th component and negative in case the mass flow rate of the pollutant decreases within the  $k$ th component.

For a determination of the environmental impact rate of  $n$  outlet streams of a component,  $n-1$  auxiliary equations have to be defined according to the F-rule and P-rule. Further information on auxiliary equations in exergoenvironmental analysis can be found in Refs. [11,22]. The environmental impact associated with the exergy destruction  $\dot{B}_{D,k}$  can be calculated according to Eq. (14)

$$\dot{B}_{D,k} = b_{F,k} \dot{E}_{D,k} \quad (14)$$

The environmental impact associated with the final product is equal to the sum of the environmental impact of the product streams leaving the overall system (methanol and electricity) and the total environmental impact of the exergy losses. In this study, the component-related environmental impact  $\dot{Y}_k$  is neglected. However, the variable is meaningful to identify the potential of

reducing the environmental impact associated with the system units. For an identification of the components with the highest environmental impact, the sum of environmental impacts associated with the pollutant formation and the exergy destruction is used ( $\dot{B}_k^{\text{PF}} + \dot{B}_{D,k}$ ). Furthermore, two exergoenvironmental variables are used to assess the improvement potential in regard to their environmental impact.

$$r_{b,k} = \frac{(b_{P,k} - b_{F,k})}{b_{F,k}} \quad (15)$$

$$f_{b,k} = \frac{(\dot{Y}_k + \dot{B}_k^{\text{PF}})}{(\dot{Y}_k + \dot{B}_k^{\text{PF}} + \dot{B}_{D,k})} \quad (16)$$

The relative difference between the specific environmental impacts associated with the exergy of product and fuel  $r_{b,k}$  (Eq. (15)) serves as an indicator for the environmental reduction potential of a component. The value of  $r_{b,k}$  can become negative when

**Table 4**  
Impact assessment for selected emissions (Eco-Indicator 99 [9,19]).

Emission	Eco-Indicator points
1 kg CO <sub>2</sub>	0.0054545
1 kg CO	0.0083636
1 kg CH <sub>4</sub>	0.1146225
1 kg CH <sub>3</sub> OH	0.002648
1 kg H <sub>2</sub>	0.83

$b_{F,k} > b_{p,k}$ , and thus the  $k$ th component may contribute to a decrease of the overall environmental impact.

The exergoenvironmental factor  $f_{b,k}$  is calculated as the ratio of the sum of the component-related environmental impact and production of pollutants ( $\dot{Y}_k + \dot{B}_k^{PF}$ ) to the sum of the environmental impacts associated with the  $k$ th component ( $\dot{Y}_k + \dot{B}_k^{PF} + \dot{B}_{D,k}$ ). Note that the value of the exergoenvironmental factor can become negative.

The values of component-related pollutant formation have to be calculated in order to set up the exergoenvironmental balances. The chemical reactions occur within the reforming unit, the water gas shift, the combustion chamber and the methanol synthesis reactor. Hence, the pollutant formation only is calculated for these components by using Eq. (17). The values for  $b_{CH_4}^{PF}$ ,  $b_{CO_2}^{PF}$ ,  $b_{CO}^{PF}$  have been retrieved from the Eco-Indicator 99 database and are summarized in Table 4.

$$\begin{aligned} \dot{B}_k^{PF} = & b_{CH_4}^{PF} (\dot{m}_{CH_4,out} - \dot{m}_{CH_4,in}) + b_{CO_2}^{PF} (\dot{m}_{CO_2,out} - \dot{m}_{CO_2,in}) \\ & + b_{CO}^{PF} (\dot{m}_{CO,out} - \dot{m}_{CO,in}) + b_{H_2}^{PF} (\dot{m}_{H_2,out} - \dot{m}_{H_2,in}) \\ & + b_{CH_3OH}^{PF} (\dot{m}_{CH_3OH,out} - \dot{m}_{CH_3OH,in}) \end{aligned} \quad (17)$$

The calculated value of the exergy of product and the exergy of fuel of each component (for the selected main components) as well as the environmental impact associated with them are provided in Tables 6 and 7. In order to calculate the environmental impact of the chemical conversion units, such as the reformer, the combustion chamber and the methanol reactor, the environmental impact rate is split into their chemical and physical parts. According to Equation (17), only the specific environmental impact of the reacting components changes within the chemical conversion units.

After solving the set of linear equations, including components balances and auxiliary equations, the environmental impact of the final products, grade AA methanol and electricity, is calculated. Furthermore, the environmental impact associated with the exergy losses  $\dot{B}_{L,tot}$ , comprising the offgas from the HRSG and the bottom product from the distillation column, is identified.

## 5. Results

### 5.1. Process performance and exergetic analysis

The key characteristics of the processes are shown in Table 5. The processes are designed based on a similar production capacity of around 2500 mtpd. However, the SMR process has an electricity capacity of 140.2 MW while the ATR process only generates a small amount of excess electricity of 4.5 MW. In regard to the SMR process, the generation of electricity is directly linked to the supply of process heat to the endothermic reforming unit. On a low temperature level, a large amount of heat is integrated into the steam cycle, resulting in a substantial electricity generation much greater than the internal demand. On the other hand, the steam cycle in the ATR process is designed to only cover the internal demand. The high process heat demand of the steam reformer can be only

**Table 5**  
Key characteristics of the SMR and ATR processes.

	Unit	SMR	ATR
CH <sub>3</sub> OH-capacity	t/d	2590	2452
Electric capacity	MW	140.2	4.5
CH <sub>4</sub> -intensity <sup>a</sup>	kg/MWh	202.0	126.1
Electric intensity <sup>b</sup>	MJ/kg	1.78	2.01
RTFR	–	5.6	5.9
CH <sub>3</sub> OH-yield	mole-%	6.0	8.0

<sup>a</sup> Ratio of total natural gas intake to the total exergy of product.

<sup>b</sup> The number includes the electric consumption along the synthesis route.

covered by combustion of an additional amount of natural gas, which is not required within the ATR process.

$$\text{CH}_4 - \text{intensity} = \frac{\dot{m}_{CH_4,Syngas} + \dot{m}_{CH_4,Fuel}}{\dot{E}_{P,tot}} \quad (18)$$

$$\text{Electric intensity} = \frac{\dot{W}_{NG \text{ comp}} + \dot{W}_{Syngas \text{ comp}} + \dot{W}_{Recycle \text{ comp}}}{\dot{m}_{Meoh}} \quad (19)$$

This design difference is represented by the CH<sub>4</sub>-intensity in Eq. (18), which is defined as the ratio of the total natural gas intake, both for the process heat generation and for the syngas production, to the exergy of products of the overall system. Accordingly, the SMR and ATR processes have a ratio of 202.0 and 126.1 kg/MWh, respectively.

Another key figure refers to the electric intensity in Eq. (19), which includes all electrical duties required for the operation of the synthesis route (required for the production of the methanol product). The electric intensity for the SMR and the ATR process is 1.78 MJ/kg and 2.01 MJ/kg, respectively. The decisive difference between the processes lies on the location of the main pressurization of the processes. In the ATR process, main compression is conducted in the natural gas compressor upstream the reformer resulting in a low size of the energy intensive syngas compression for bridging the pressure difference between the reformer and the synthesis unit. In contrast, in the SMR process the syngas compression unit represents a large energy consumer due to large pressure difference. Finally, the multistage air compressor within the ASU is adding a large value to the electric intensity of the ATR process.

Due to unfavorable syngas composition, the methanol yield is in a low range of 6.0–8.0%, resulting a large recycle-to-feed-ratio (RTFR) of 5.6 and 5.9, respectively.

The results of the exergetic analysis for selected components and the overall system are presented in Tables 6 and 7. The SMR process with high CH<sub>4</sub>-intensity has an overall exergetic efficiency of 34.8%, while the ATR process without fuel demand has an efficiency of 56.9%. The large difference in the overall efficiency is not only caused by a different performance of the synthesis, but is mainly caused by the extent of the inefficiencies within the steam cycle.

### 5.2. Exergoenvironmental analysis

Application of the exergoenvironmental analysis shows that the specific environmental impact per unit of exergy of generated methanol is 6.95 mPt/MJ and 6.6 mPt/MJ for the processes using steam reforming and autothermal reforming. On a mass base the methanol product has an environmental impact equal to 156.4 mPt/kg and 134.0 mPt/kg for the SMR and ATR process, respectively. Based on the lower heating value LHV of 20.1 MJ/kg, the

**Table 6**  
Results obtained from the exergy and the exergoenvironmental analysis for selected components of the SMR plant.

Component	Exergy analysis ( $\dot{E}_{L,tot} = 194.81$ MW)					Exergoenvironmental analysis ( $\dot{B}_{L,tot} = 1,009.3$ mPt/s)					
	$\dot{E}_{F,k}$	$\dot{E}_{P,k}$	$\dot{E}_{D,k}$	$\epsilon_k$	$\gamma_k$	$\dot{B}_k^{PF}$	$\dot{B}_{D,k}$	$\dot{B}_k^{PF} + \dot{B}_{D,k}$	$b_{F,k}$	$b_{P,k}$	$r_{b,k}$
	(MW)	(MW)	(MW)	(%)	(%)	(mPt/s)	(mPt/s)	(mPt/s)	(mPt/MJ)	(mPt/MJ)	(%)
R-04**	1,105.41	968.73	36.67	96.35	1.57	3,864.88	59.23	3,924.11	1.62	5.67	250.81
E-06	97.77	40.14	57.64	41.05	2.47	0.00	3,017.86	3,017.86	52.36	127.55	143.60
HP-EVA	436.16	324.87	111.29	74.48	4.77	0.00	915.68	915.68	8.23	11.05	34.26
T-02	380.36	350.22	30.14	92.08	1.30	0.00	578.20	578.20	19.19	20.84	8.61
C-03	16.11	7.88	8.23	48.91	0.35	0.00	565.40	565.40	68.68	140.42	104.46
E-04	64.69	53.25	11.44	82.32	0.49	0.00	487.01	487.01	42.57	51.72	21.48
CM-02	203.86	181.70	22.16	89.13	0.95	0.00	461.67	461.67	20.84	23.38	12.19
LP-EVA	107.72	60.79	46.93	56.43	2.01	0.00	386.13	386.13	8.23	14.58	77.21
E-08	23.14	15.20	7.94	65.70	0.34	0.00	337.91	337.91	42.58	64.80	52.21
HP-SH	129.89	92.85	37.04	71.48	1.59	0.00	304.78	304.78	8.23	11.51	39.90
E-02	50.54	45.45	5.09	89.93	0.22	0.00	266.40	266.40	52.36	58.22	11.19
R-03	45.11	44.13	0.98	97.82	0.04	89.86	104.04	193.90	105.95	110.36	4.15
LP-EVA	28.14	7.36	20.78	26.16	0.89	0.00	170.93	170.93	8.23	31.45	282.22
E-07	4.35	2.08	2.27	47.84	0.10	0.00	99.13	99.13	43.65	91.25	109.04
R-04 <sup>a</sup>	1,669.71	970.2	699.51	58.11	29.97	-4,157.33	3,866.83	-290.50	5.53	5.23	-54.42
<b>Overall system</b>	<b>2,334.39</b>	<b>812.54</b>	<b>1,327.88</b>	<b>34.81</b>	<b>56.88</b>	<b>-4,206.70</b>	<b>7,028.77</b>	<b>2,822.06</b>	<b>5.29</b>	<b>10.03</b>	<b>89.60</b>

<sup>a</sup> Furnace of the steam reforming unit \*\* Tubular reformer.

**Table 7**  
Results obtained from the exergy and the exergoenvironmental analysis for the ATR plant.

Component	Exergy analysis ( $\dot{E}_{L,tot} = 1,144.3$ MW)					Exergoenvironmental analysis ( $\dot{B}_{L,tot} = 230.6$ mPt/s)					
	$\dot{E}_{F,k}$	$\dot{E}_{P,k}$	$\dot{E}_{D,k}$	$\epsilon_k$	$\gamma_k$	$\dot{B}_k^{PF}$	$\dot{B}_{D,k}$	$\dot{B}_k^{PF} + \dot{B}_{D,k}$	$b_{F,k}$	$b_{P,k}$	$r_{b,k}$
	(MW)	(MW)	(MW)	(%)	(%)	(mPt/s)	(mPt/s)	(mPt/s)	(mPt/MJ)	(mPt/MJ)	(dimensionless)
R-03	1,032.23	955.89	76.34	92.60	6.67	2,280.45	872.29	3,099.48	10.73	13.97	30.22
E-03	52.37	39.54	12.83	75.49	1.12	0.00	797.00	797.00	62.10	82.26	32.46
E-08	15.52	4.59	10.93	29.58	0.96	0.00	472.52	472.52	43.23	146.13	238.04
E-02	25.33	19.03	6.30	75.12	0.55	0.00	391.40	391.40	62.10	82.67	33.12
E-05	14.34	8.07	6.27	56.29	0.55	0.00	332.39	332.39	53.04	94.24	77.67
R-04	71.00	61.38	9.62	86.46	0.84	241.23	80.87	322.10	8.41	13.66	62.39
E-10	27.60	23.53	4.07	85.25	0.36	0.00	193.75	193.75	47.59	55.83	17.30
HP-EVA	61.15	47.84	13.31	78.23	1.16	0.00	75.28	75.28	5.65	7.23	27.83
CM-02	69.41	61.92	7.48	89.22	0.65	0.00	67.59	67.59	9.03	10.13	12.08
T-01	76.43	69.31	7.12	90.68	0.62	0.00	57.77	57.77	8.11	8.95	10.28
HP-SH	48.26	38.50	9.76	79.78	0.85	0.00	55.18	55.18	5.65	7.09	25.35
R-09	308.90	175.74	133.16	56.89	11.64	-1,480.62	861.69	-618.93	6.47	2.95	-54.42
<b>Overall system</b>	<b>1,144.30</b>	<b>651.15</b>	<b>453.49</b>	<b>56.90</b>	<b>39.63</b>	<b>-2,166.66</b>	<b>2,558.83</b>	<b>392.17</b>	<b>5.64</b>	<b>6.58</b>	<b>16.68</b>

environmental impact of methanol is 7.79 mPt/MJ and 6.67 mPt/MJ.

The generated electricity has an environmental impact of 88.8 Pt/MWh for the SMR process and 65.3 Pt/MWh for the ATR process. These numbers result when the environmental impact associated with the exergy losses of the overall system is charged to the products. In the SMR case,  $\dot{B}_{L,tot}$  is equals 1009.3 mPt/s, while  $\dot{B}_{L,tot}$  has a value of 230.6 mPt/s for the ATR process.

The term of the pollutant formation has a major influence on the environmental impact associated with the product streams. Excluding the impact of  $\dot{B}_k^{PF}$ , the methanol and electricity generated by the SMR process have an environmental impact of 284.6 mPt/kg (15.2 mPt/MJ) and 98.2 Pt/MWh. Accordingly, methanol and electricity generated by the ATR process have an environmental impact 207.6 mPt/kg (9.3 mPt/MJ) and 71.3 Pt/MWh. Consequently, the chemical conversion units within the synthesis route lead to a reduction of the total environmental impact associated with the products. Since neither methanol nor methane are emitted, their inclusion in the pollution term  $\dot{B}_k^{PF}$  can be questioned.

The results of the exergoenvironmental analysis for selected components of the SMR and the ATR process are presented in Tables 6 and 7. The components are listed in descending order of their total environmental impact as the components with a high value of  $\dot{B}_k^{PF} + \dot{B}_{D,k}$  should be considered first to reduce the overall

environmental impact.

A comparison of the results of both processes shows, that the environmental impact of the components in the SMR process is of a larger magnitude due to large exergy destruction occurring within the components. Considering Table 6, the tubular reformer R-04 has the largest environmental impact due to the formation of the pollutants carbon monoxide and hydrogen. The impact of  $\dot{B}_{D,k}$  is marginal since the specific environmental impact per unit of exergy of fuel is low. A reduction of the pollutant formation by lowering the S/C ratio could be achieved at the expense of a higher methane leak. Another measure to decrease the pollutant formation of this unit is the operation at higher temperatures and under a low pressure of 5 bar and less. This measure would cause a shift of the H<sub>2</sub>/CO ratio to lower values and thus an impact reduction of around 3–5%. Nevertheless, the disadvantages of a higher power consumption in the syngas compression unit and a non-ideal syngas composition would be significant.

The syngas cooler E-06 is rated to position number two and has a large environmental impact due to high specific impact at which the exergy of fuel is destroyed. In general, for both processes, the syngas cooler and the intermediate cooler in the syngas compression unit (E-06 and E-07 in the SMR process and E-03, E-02 and E-05 in the ATR process) have a large value for  $\dot{B}_{D,k}$  caused by a large

exergy destruction due to heat transfer at high temperature difference. A graded heat transfer in several heat exchangers with lower temperature difference between the warm and cold side would reduce the environmental impact within the cooling units.

The HRSG in the SMR process, including the HP-EVA, HP-SH, LP-EVA, has a large environmental impact associated with exergy destruction. The same applies to the HRSG of the ATR process, especially to the heat exchangers within the high-pressure level (HP-EVA and HP-SH). The components offer a high potential for environmental improvement by decreasing their exergy destruction. This can for example be achieved by an improvement of the heat integration to reduce the average temperature difference of heat transfer.

Considering the SMR process, the expander T-02 and the distillation column C-03 are rated to position number four and five. T-02 has a large exergy destruction while the ecologic significance of C-03 is mainly caused by the high specific environmental impact per unit of exergy of fuel. An environmental improvement related to the impact of the exergy destruction can be achieved by using turbomachinery with a higher isentropic efficiency. With respect to C-03, a decrease of the value of the reflux ratio might reduce the exergy destruction and thus the associated environmental impact.

A reduction of the environmental impact of the turbine T-01 and the compressor C-02 can be achieved through an investment in modern equipment with high isentropic efficiency. The furnace R-04, representing the component with the highest exergy destruction, only is rated to position number four. The sum  $\dot{B}_k^{\text{PF}} + \dot{B}_{D,k}$  is small since the large environmental impact associated with the exergy destruction is reduced by the negative value of the pollutant formation  $\dot{B}_k^{\text{PF}}$ , which results from the consumption of CH<sub>4</sub>.

Considering the results for the ATR process in Table 7, the combustion unit of the autothermal reformer has an outstandingly high environmental impact, resulting from the formation of hydrogen and carbon monoxide. An adjustment of the operation conditions with lower steam-to-carbon ratio leads to a reduction of the environmental impact due to a decrease in exergy destruction and pollutant formation. For instance, changing the S/C ratio from 0.6 to 0.5 would reduce the environmental impact of the ATR by 10%. Furthermore, sensitivity analyses showed that the environmental impact related to exergy destruction peaks for a O/C ratio of 0.5 regardless of the S/C-ratio.

The value of  $\dot{B}_{D,k}$  of the crude product cooler E-08 within the synthesis unit (rated to position number three) is caused by the large heat transfer rate (84 MW) at an average temperature difference of approximately 50 °C. A decrease of the mass flow on the cold side would reduce the average temperature difference and thus improve the component from an exergoenvironmental point of view. The catalytic zone of the autothermal reformer R-04, carrying out the reforming and water gas shift reactions, has an environmental impact related to pollutant formation and exergy destruction. The pollutant formation  $\dot{B}_k^{\text{PF}}$  of the component is caused by the conversion of 10% of the methane intake to hydrogen and carbon monoxide. A reduction of the environmental impact  $\dot{B}_{D,k}$  of R-04 is achieved by an increase of the operating temperature due an increase of the O/C ratio in the combustion zone.

The recuperator E-10 has an environmental impact mainly due to exergy destruction, being caused by a large heat transfer rate associated with large recycle streams. An adjustment of the temperature level on the hot side through an increase of the cooling duty within the reactor reduces the environmental impact related to exergy destruction.

The combustion unit R-09 represents another outstanding component, having a large negative value for the pollutant formation  $\dot{B}_k^{\text{PF}}$ . The component therefore decreases the environmental impact of the overall system. The impact of all other components,

including the air compressor CM-02, the distillation columns (C-01 – C-03) and the turbomachinery (T-01 – T-03), is marginal.

A comparison of the results for the processes shows that the overall environmental impact  $\dot{B}_{\text{tot}}^{\text{PF}} + \dot{B}_{D,\text{tot}}$  for the ATR process is low compared to the SMR process. This is mainly caused by the difference in exergetic efficiency (ATR process 56.9% and SMR process 34.8%) and thus due to the environmental impact associated with the exergy destruction. An improvement strategy (reduction of the overall environmental impact) should first consider changes of the operating parameters of the reforming unit and the combustion unit (R-04\* and R-04\*\* in the SMR process and R-03, R-04 and R-09 in the ATR process), as these components significantly determine the overall environmental impact due to exergy destruction and pollutant formation. For a selection of suitable operation parameters, such as the H/C ratio, O/C ratio, temperature and pressure, further sensitivity analyses for the dependence of  $\dot{B}_k^{\text{PF}} + \dot{B}_{D,k}$  should be performed.

## 6. Conclusions

This study discusses the environmental impact of commercial methanol production synthesis routes via syngas production by steam reforming and autothermal reforming. For the first time, an exergoenvironmental analysis is applied to this kind of chemical value chain. In general, the analysis reveals the formation of environmental impacts associated with the components of chemical and energetic conversion systems and provides useful information for reducing the environmental impact of the design.

The analysis shows that the components with a high environmental impact are manifold. The environmental impact is caused by exergy destruction occurring within the components while the pollutant formation  $\dot{B}_k^{\text{PF}}$  within the chemical conversion units reduces the environmental impact associated with the overall system ( $\dot{B}_{k,\text{tot}}^{\text{PF}} + \dot{B}_{D,\text{tot}}$ ). Thus, the total environmental impact can be lowered by a reduction of the exergy destruction within the components using for instance the latest equipment technology and materials with improved properties. Furthermore, small changes in the operating conditions, such as the S/C and O/C ratio, may lead to a larger negative value of the pollutant formation and thus to a considerable reduction of the overall environmental impact.

The turbomachinery including the recycle compressors might be substituted by equipment which has a higher isentropic efficiency. Furthermore, the progress in material science allows live steam temperatures of up 630 °C which would decrease the exergy destruction and thus also the environmental impact  $\dot{B}_D$  of steam turbine and the syngas coolers considered within this study. With respect to the heat exchangers, metal alloys (based on steel, aluminum and copper) can be used instead of conventional steel sheets to increase the thermal efficiency lowering the material and fuel consumption.

For future research, life cycle assessment and exergoenvironmental analyses will be conducted for advanced processes using mixed reforming of natural gas and for processes with carbon capture and utilization. Furthermore, an advanced exergoenvironmental analysis would provide additional information on the components interactions, thus demonstrating further reduction potential in relation to the environmental impact.

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