

# Impurity impacts on the purification process in oxy-fuel combustion based CO<sub>2</sub> capture and storage system

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## ABSTRACT

Based on the requirements of CO<sub>2</sub> transportation and storage, non-condensable gases, such as O<sub>2</sub>, N<sub>2</sub> and Ar should be removed from the CO<sub>2</sub>-stream captured from an oxy-fuel combustion process. For a purification process, impurities have great impacts on the design, operation and optimization through their impacts on the thermodynamic properties of CO<sub>2</sub>-streams. Study results show that the increments of impurities will make the energy consumption of purification increase; and make CO<sub>2</sub> purity of separation product and CO<sub>2</sub> recovery rate decrease. In addition, under the same operating conditions, energy consumptions have different sensitivities to the variation of the impurity mole fraction of feed fluids. The isothermal compression work is more sensitive to the variation of SO<sub>2</sub>; while the isentropic compression work is more sensitive to the variation of Ar. In the flash system, the energy consumption of condensation is more sensitive to the variation of Ar; but in the distillation system, the energy consumption of condensation is more sensitive to the variation of SO<sub>2</sub>, and CO<sub>2</sub> purity of separation is more sensitive to the variation of SO<sub>2</sub>.

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## 1. Introduction

Oxy-fuel combustion is one of the promising approaches to CO<sub>2</sub> capture [1–5]. Since the combustion takes place in a low-nitrogen environment, it produces a flue gas that consists of mainly H<sub>2</sub>O and CO<sub>2</sub>. Therefore a simplified flue gas processing (CO<sub>2</sub> processing), which is essential to achieve a low cost for CO<sub>2</sub> capture, can be used instead of conventional means of CO<sub>2</sub> capture, like chemical absorption [6]. Fig. 1 shows the process scheme of CO<sub>2</sub> capture and storage (CCS) system based on oxy-fuel combustion capture. After preliminary flue gas cleaning, the flue gas contains around 75% [7] by volume CO<sub>2</sub> at atmosphere pressure. Firstly it is necessary to remove H<sub>2</sub>O to reduce corrosion and to avoid ice or hydrate formation in the following processing steps. The moisture removal is achieved by compressed moisture condensation and dehydration, which are combined with initial CO<sub>2</sub> compression. After drying, the CO<sub>2</sub>-stream may go through a purification/liquefaction procedure, in which the non-condensable gases such as N<sub>2</sub>, O<sub>2</sub> and Ar will be separated by physical separation to give >95 mol% of CO<sub>2</sub> [7]. Here compression, dehydration and purification/liquefaction are so-called CO<sub>2</sub> processing, which purpose is to provide a dense/liquid CO<sub>2</sub>-stream for economic transport and storage,

and to meet a specification required by operation and safety. Finally CO<sub>2</sub>-streams will be transported to storage reservoir by vessels or pipeline.

Compared with other approaches for CO<sub>2</sub> capture, such as pre-combustion capture and post-combustion capture, relatively high levels of impurities are expected in the captured CO<sub>2</sub>-stream from oxy-fuel combustion [5,7–9]. So it presents more challenges for the flue gas cleaning and processing procedures [6]. Oryshchyn [10] and White [11] have studied the processes of cleaning SO<sub>2</sub> and NO<sub>x</sub>; here we mainly focus on the removal of non-condensable gases.

Our previous results [12] show that impurities will affect the thermodynamic properties of CO<sub>2</sub>-fluids greatly, and further affect on the design and operation of different CCS processes. Since the purification involves more significant phase changes of CO<sub>2</sub>-streams, it is more meaningful to understand the impurity impacts on the purification process. However only a few of preliminary studies were addressed so far [13,14].

This paper is to investigate the impurity impacts on the CO<sub>2</sub> purification in the oxy-fuel combustion based CCS system, including the impurity impacts on the thermodynamic properties of CO<sub>2</sub>-streams under the operating conditions of purification, and the impurity impacts on the system parameters, such as the operation conditions of separation, the energy consumption of compression and condensation, CO<sub>2</sub> purity of the purification product and CO<sub>2</sub> recovery rate, which is defined as

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### Nomenclature

$a, b$	parameters in Peng–Robinson EOS
$C, c$	heat capacity
$H, h$	enthalpy
$P$	pressure
$R$	gas constant
$S, s$	entropy
$T$	temperature
$v$	molar volume
$W, w$	work
$x$	mole fraction in liquid phase
$X$	total mole fraction
$y$	mole fraction in vapor phase
$\alpha_{AB}$	relative volatility
$\eta$	efficiency

CRR	CO <sub>2</sub> Recovery Rate
DP	dew point
GERG	GERG EOS
EOS	equation of state
PSRK	Predictive–Redlich–Kwong–Soave
VLE	vapor liquid equilibrium

### Subscripts

Ae, Be	component labels
i	component labels
p	isobaric
S	isentropic
T	isothermal

### Abbreviations

BP	bubble point
CCS	CO <sub>2</sub> capture and storage

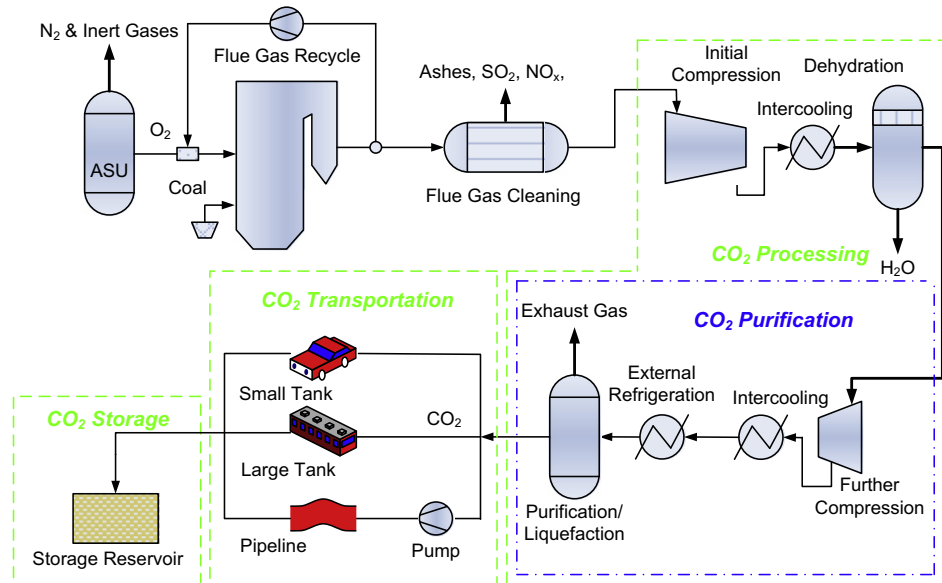


Fig. 1. Process scheme of CCS system based on oxy-fuel combustion capture.

$$\text{CRR} = \frac{(\text{Mole flow} \times \text{CO}_2 \text{ Mole fraction})_{\text{Production}}}{(\text{Mole flow} \times \text{CO}_2 \text{ Mole fraction})_{\text{Feed}}} \quad (1)$$

Two configurations of purification were analyzed, including flash and distillation. The comparison results give some insights to and guidelines regarding the design and optimization for CO<sub>2</sub> purification system.

## 2. Impurity impacts on thermodynamic properties

Normally the purification process includes three steps: CO<sub>2</sub>-stream compression, CO<sub>2</sub>-stream condensation and non-condensable gas separation. By changing the thermodynamic properties of CO<sub>2</sub>-mixtures, impurities have great impacts on system design, operation and optimization. In Table 1, we summarized the relationships between thermodynamic properties and some system parameters of CO<sub>2</sub> purification. For example: the variation of impurity content would vary the VLE properties of CO<sub>2</sub>-mixtures, which mainly mean the boiling and condensing behaviors. Since the

Table 1

The relationship between thermodynamic properties and purification parameters

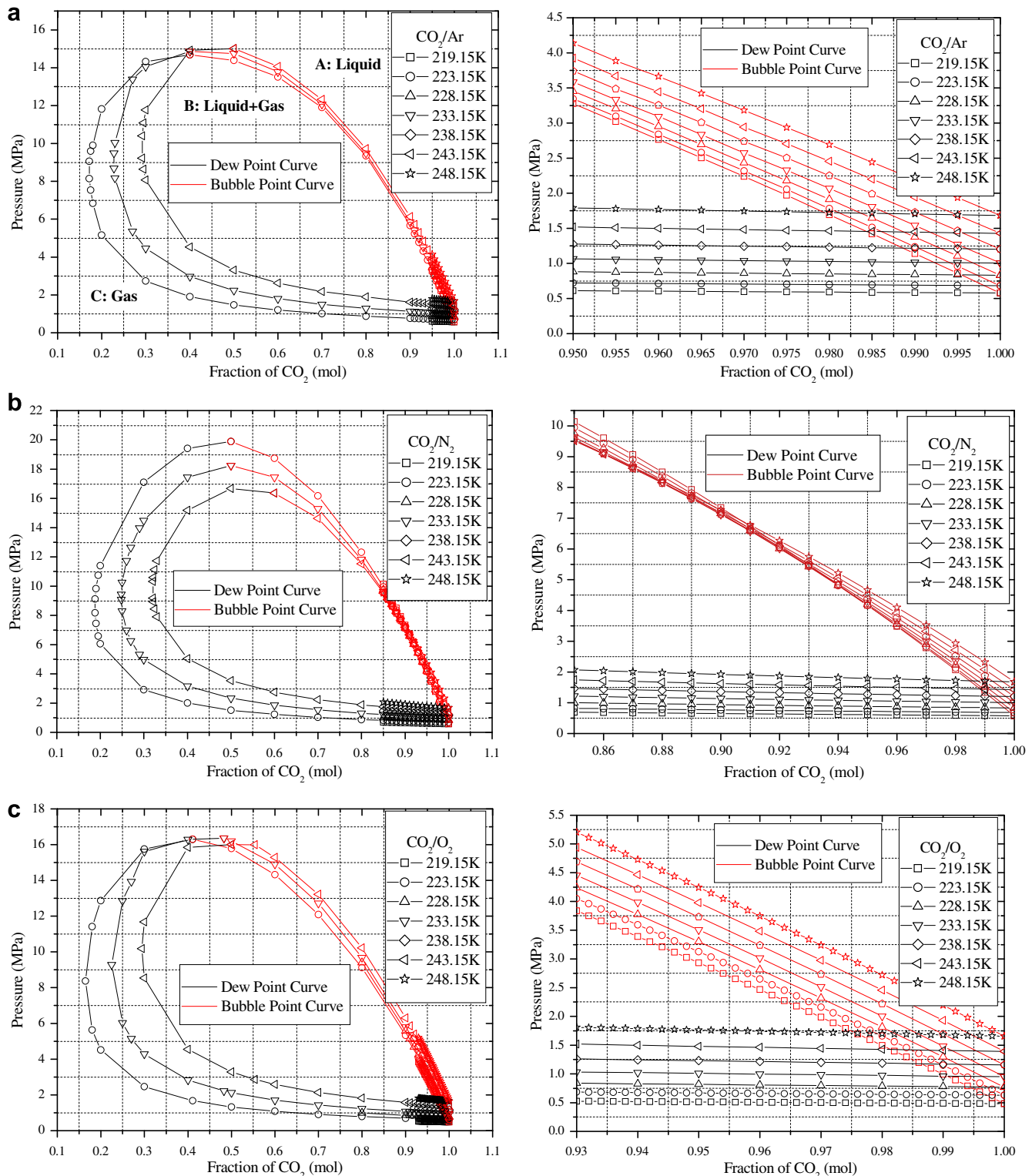
		Operation conditions	Energy consumption	Configuration	Separation performance
VLE	Dew point (DP)	✓	✓		
	Bubble point (BP)	✓	✓		✓
	Difference of DP and BP	✓	✓	✓	
	Heat capacity		✓		
	Enthalpy and entropy		✓		

physical separation can only be carried out above the mixture's condensing pressure, or below its condensing temperature, when the VLE properties are changed, correspondingly the operation conditions of the CO<sub>2</sub> compression/purification (e.g. the discharge pressure of compression and the condensation temperature)

**Table 2**  
Calculation methods for the thermodynamic properties of different CO<sub>2</sub>-mixtures

	VLE	Enthalpy	Entropy
CO <sub>2</sub> /O <sub>2</sub>	PSRK	GERG2004	GERG2004
CO <sub>2</sub> /N <sub>2</sub>	GERG2004	GERG2004	GERG2004
CO <sub>2</sub> /Ar	GERG2004	GERG2004	GERG2004
CO <sub>2</sub> /SO <sub>2</sub>	–	PSRK	PSRK

should also be changed. Since the CO<sub>2</sub> purity of the separation product is the CO<sub>2</sub> mole fraction of saturated liquid, when the boiling behavior is changed, the performance of separation would be changed. In addition the variation of impurity content would also vary the enthalpy, entropy and heat capacity of CO<sub>2</sub>-mixtures. Since the energy consumptions of compression and refrigeration are decided by the enthalpy and entropy changes in those



**Fig. 2.** Phase diagrams of CO<sub>2</sub>/Ar, CO<sub>2</sub>/N<sub>2</sub>, and CO<sub>2</sub>/O<sub>2</sub> based on the temperature and composition ranges of purification.

processes, as a result, impurities would affect the energy consumption. Therefore in order to understand the impurities' impacts on the purification system, their impacts on the thermodynamic properties must be known previously.

Generally the main impurities from oxy-fuel combustion are water, non-condensable gases, such as  $N_2$ ,  $O_2$  and Ar, and  $SO_2$  [6]. Since the moisture ( $H_2O$ ) has been removed before the purification procedure, only the impurities,  $N_2$ ,  $O_2$ , Ar and  $SO_2$ , are studied in this paper. The possible ranges of impurity mole fraction are: Ar (0–5%),  $N_2$  (0–15%),  $O_2$  (0–7%) and  $SO_2$  (0–1.5%). In order to analyze the impacts of impurities reasonably, the possible temperature and pressure windows are defined based on the operation conditions of the  $CO_2$  purification: the temperature range: 218.15 to 248.15 K and pressure range: 2 to 5 MPa [7]. To pursue high accuracy, vari-

ous EOS have been used to calculate the thermodynamic properties of different  $CO_2$ -mixtures. According to the evaluation of the calculation methods on the thermodynamic properties of  $CO_2$  and  $CO_2$ -mixtures [15–17], PSRK [18] and GERG2004 EOS [19] were employed to do the calculations in this study. More details are summarized in Table 2.

### 2.1. Impacts on VLE

Phase diagrams of binary  $CO_2$ -mixtures, like  $CO_2$ /Ar,  $CO_2$ / $N_2$  and  $CO_2$ / $O_2$  are shown in Fig. 2. In the area marked A, both  $CO_2$  and impurities are in the liquid phase; in the area marked as C, they are in the gas phase; in the area marked as B, which is between A and C, two phases co-exist.

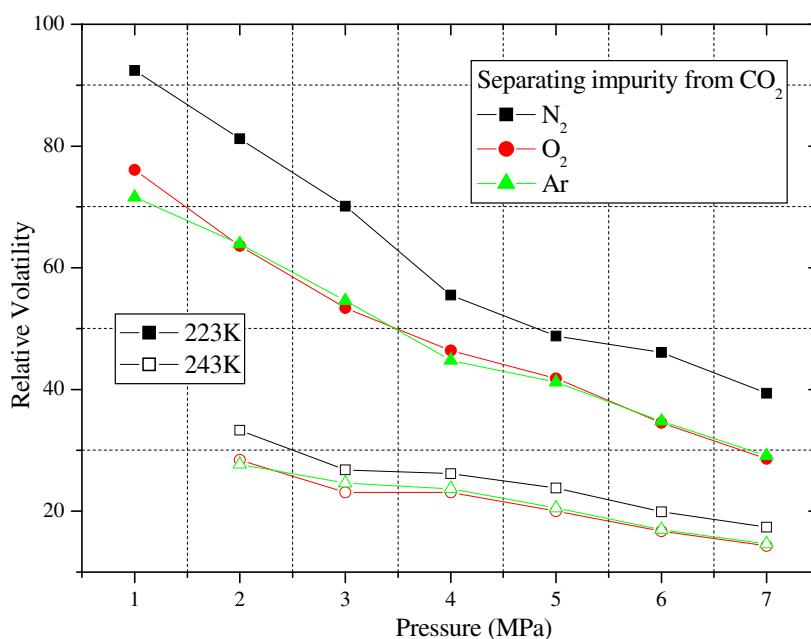


Fig. 3. The relative volatilities of the non-condensable components regarding  $CO_2$ .

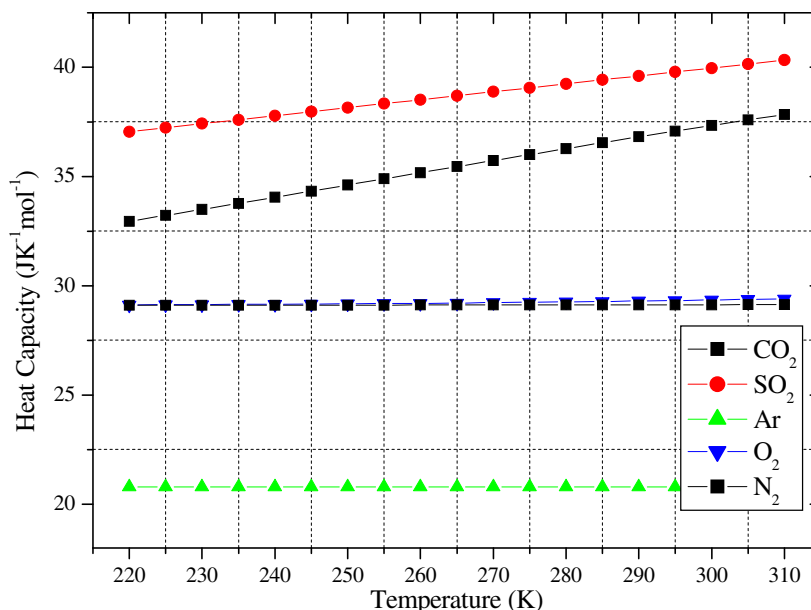


Fig. 4. Heat capacity of different components at different temperatures.

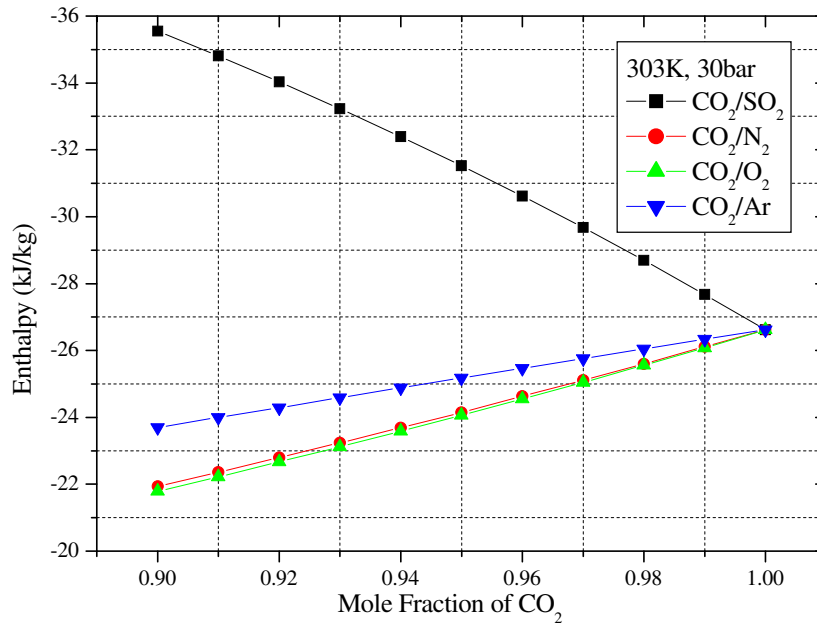


Fig. 5. Enthalpies of different CO<sub>2</sub>-mixtures in gas phase.

Compared with the saturated state of pure CO<sub>2</sub>, it is quite clear that the increment of non-condensable gases makes both the boiling pressure and condensing pressure of CO<sub>2</sub>-mixtures rise. And at high purity of CO<sub>2</sub>, for example CO<sub>2</sub> > 70 mol%, impurities have more remarkable impacts on bubble point than on dew point as indicated on the right side of Fig. 2.

The dew points of CO<sub>2</sub>-mixtures determine the operating conditions of purification. Although non-condensable impurities have quite similar impacts on the dew points of CO<sub>2</sub>-mixtures, comparatively the variation of N<sub>2</sub> impacts are bigger than those of O<sub>2</sub> and Ar. At a certain temperature, for example 223.15 K, if the impurities increase from 0 mol% to 5 mol%, the condensing pressure is increased by 0.429 bar by N<sub>2</sub>, 0.423 bar by O<sub>2</sub> and 0.424 bar by Ar, compared with pure CO<sub>2</sub>. It implies that condensing CO<sub>2</sub>-streams containing N<sub>2</sub> may be more difficult compared with other impurities with the same concentration. In addition, if the impurity mole fractions are within their possible ranges mentioned above, the dew point curves of all binary CO<sub>2</sub>-mixtures at different temperatures are almost linear and parallel, which means the increment of condensing pressure is approximately proportional to the mole fraction of impurities.

The bubble points of CO<sub>2</sub>-mixtures determine the purity of purification product, because the CO<sub>2</sub> mole fraction in saturated liquid is the CO<sub>2</sub> purity of the purification products. From Fig. 2, it is easy to see that at a certain temperature, the saturated mole fractions of CO<sub>2</sub> in the liquid phase of CO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/O<sub>2</sub> and CO<sub>2</sub>/Ar go down along with the increment of pressure almost linearly. This means that the purity of CO<sub>2</sub> products is inverse proportion to the operating pressure that the higher the operating pressure is, the lower the CO<sub>2</sub> purity of product is. Comparatively the CO<sub>2</sub> purity of the purification products from separating CO<sub>2</sub>/N<sub>2</sub> is less sensitive to the change of operating conditions than those from separating CO<sub>2</sub>/O<sub>2</sub> and CO<sub>2</sub>/Ar. For example at 223.15 K, if operating pressure is increased by 1 MPa, for the separation of CO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/O<sub>2</sub> and CO<sub>2</sub>/Ar, CO<sub>2</sub> purity in liquid phase is decreased by around 1.53%, 2.0% and 1.9%, respectively. In addition, in the possible impurity concentration ranges all bubble point curves at different temperatures are parallel, except those of CO<sub>2</sub>/N<sub>2</sub>. This implies CO<sub>2</sub> purity of the purification products may be increased by raising operating temperature, except separating CO<sub>2</sub>/N<sub>2</sub>.

The difference between bubble and dew point indicates how easily the impurity could be separated. McCabe [20] points out that the mixtures with wide temperature differences can be separated easily. In addition, another parameter: relative volatility can be used to evaluate if the impurity could be separated. Relative volatility is defined as [20]

$$\alpha_{AB} = \frac{y_{Ae}/x_{Ae}}{y_{Be}/x_{Be}} \quad (2)$$

where  $\alpha_{AB}$  is the relative volatility of component A compared to component B when the two component mixture under equilibrium conditions,  $y_{Ae}$  is the mole fraction of component A in vapor,  $x_{Ae}$  is the mol fraction of component A in liquid phase,  $y_{Be}$  and  $x_{Be}$  are the mol fractions of component B in vapor and liquid phase, respectively. Fig. 3 shows the relative volatilities of the non-condensable components regarding CO<sub>2</sub>. All of these display that N<sub>2</sub> could be much easily separated from the CO<sub>2</sub>-mixtures compared to the separation of Ar and O<sub>2</sub>.

SO<sub>2</sub> has opposite impacts on the VLE properties of CO<sub>2</sub>-mixtures compared with O<sub>2</sub>, N<sub>2</sub> and Ar, because it would be condensed with CO<sub>2</sub>. This means that SO<sub>2</sub> will exist in the purification process studied here. Since SO<sub>2</sub> has a higher critical point than CO<sub>2</sub>, the presence of SO<sub>2</sub> in CO<sub>2</sub>-mixtures will increase the condensing

Table 3  
Basic parameters of compression

Parameters	Value
Compression type	Isothermal and isentropic
Stage	Single
Isentropic efficiency	85%
Suck $T$ and $P$	293.15 K and 0.1013 MPa
Discharging $P$	3 MPa
Discharging $T$ of cooling	293.15 K
Flow rate	600 kg/h [24]
Reference composition (mol) [7]	
CO <sub>2</sub>	76%
O <sub>2</sub>	6% ( $\pm 3\%$ )
N <sub>2</sub>	15% ( $\pm 7\%$ )
Ar	2.5% ( $\pm 2\%$ )
SO <sub>2</sub>	0.5% (0–1.5%)

temperature if the pressure is constant; or decrease the condensing pressure if the temperature is constant.

## 2.2. Impacts on the heat capacity

Heat capacity is a key parameter in the enthalpy and entropy calculation, so it is tightly related to the energy consumption of refrigeration. For mixtures, it can be calculated by

$$C_{\text{mixture}} = \sum_i^n C_i \times X_i \quad (3)$$

where  $C_i$  is the heat capacity of pure component. There is an empirical equation on calculations of heat capacity [21].

$$C = C_1 + C_2 \left[ \frac{C_3}{T} / \sinh \left( \frac{C_3}{T} \right) \right]^2 + C_4 \left[ \frac{C_5}{T} / \cosh \left( \frac{C_5}{T} \right) \right]^2 \quad \text{J/(kmol K)} \quad (4)$$

Fig. 4 shows the heat capacities ( $C_i$ ) of different pure substances at different temperatures. It indicates that  $C_{\text{SO}_2}$  is larger than  $C_{\text{CO}_2}$ , while  $C_{\text{Ar}}$ ,  $C_{\text{N}_2}$  and  $C_{\text{O}_2}$  are smaller than  $C_{\text{CO}_2}$ . At the same operating temperature, the presence of  $\text{SO}_2$  will increase; while the presence of Ar,  $\text{O}_2$  and  $\text{N}_2$  will lower the heat capacities of  $\text{CO}_2$ -mixtures ( $C_{\text{mix}}$ ). Therefore, more heat duty is needed when cooling or heating the  $\text{CO}_2$ -mixtures containing  $\text{SO}_2$  than the  $\text{CO}_2$ -mixtures containing Ar,  $\text{O}_2$  and  $\text{N}_2$ . Moreover  $C_{\text{Ar}}$  does not change with temperature compared with  $C_{\text{CO}_2}$  and  $C_{\text{SO}_2}$ ; and  $\text{O}_2$  and  $\text{N}_2$  have quite similar heat capacities, which are impacted by temperature slightly.

## 2.3. Impacts on enthalpy

Fig. 5 shows the calculated enthalpies of different  $\text{CO}_2$ -mixtures at 303 K and 30 bar. It is clear that only  $\text{SO}_2$  increases  $\text{CO}_2$ -mixture's enthalpy, which is mainly due to its higher heat capacity than that of  $\text{CO}_2$ . However, the enthalpy and entropy changes during the process are more important than the absolute enthalpy and

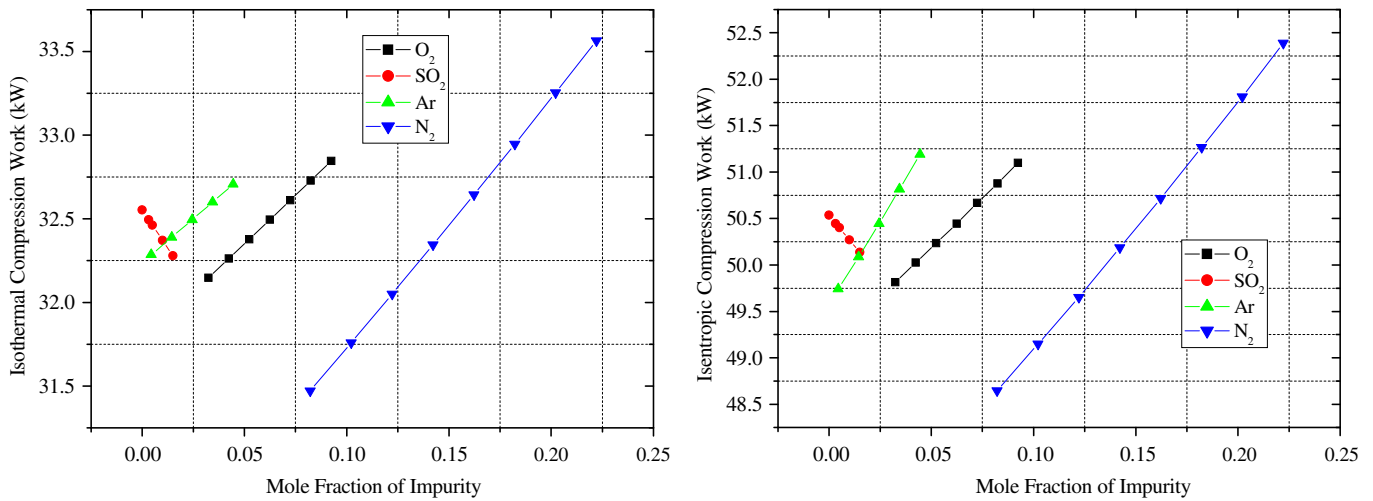


Fig. 6. Isothermal compression work and isentropic compression work at different compositions.

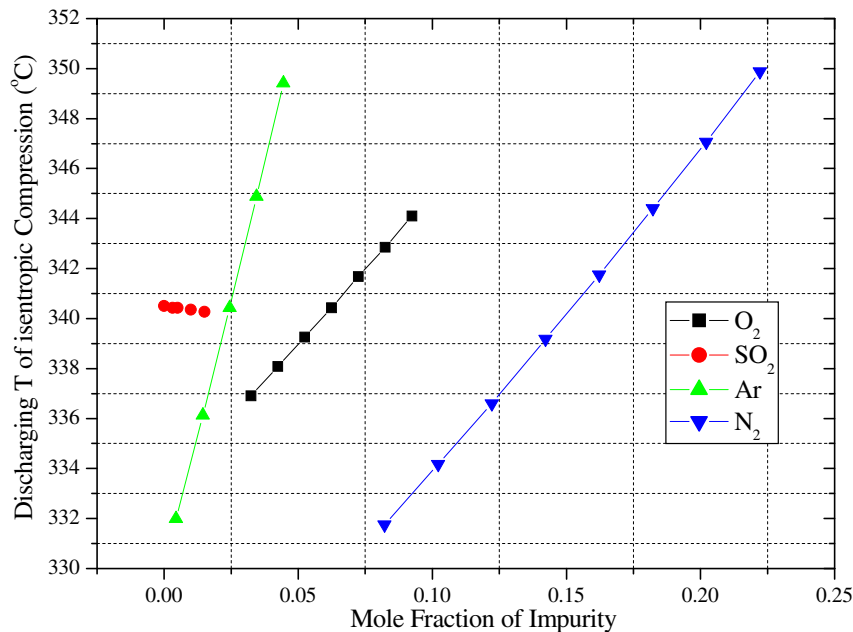


Fig. 7. Discharging temperature of isentropic compression at different compositions.



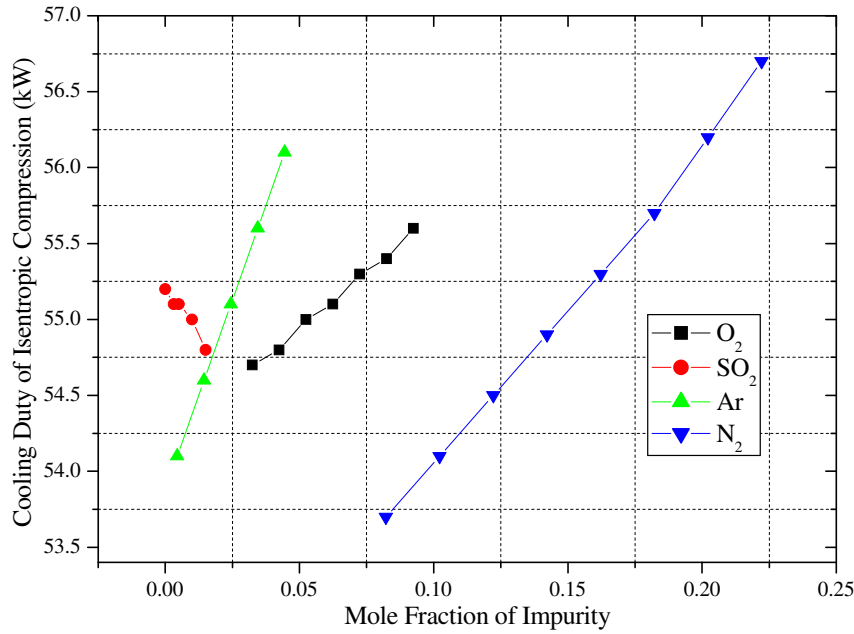


Fig. 8. Cooling duty required by isentropic compression.

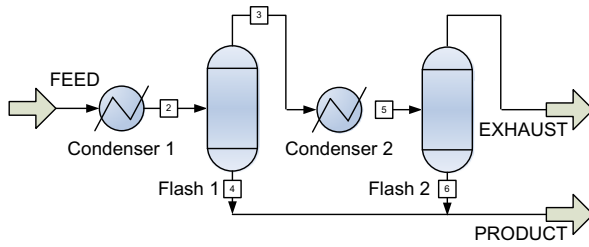


Fig. 9. Process flow-sheet diagram of 2-stage-flash system.

**Table 4**  
Parameters of 2-stage-flash system

Parameters	Value
Flow rate	600 kg/h
Stage	2
Temperature of FEED	293.15 K
Operating pressure	3 MPa
Discharging temperature of Condenser 1	248.15 K
Discharging temperature of Condenser 2	218.15 K
Reference composition of FEED (mol%)	
CO <sub>2</sub>	76%
O <sub>2</sub>	6% (±3%)
N <sub>2</sub>	15% (±7%)
Ar	2.5% (±2%)
SO <sub>2</sub>	0.5% (0–1.5%)

entropy values. Therefore more discussion about the impacts of impurities on enthalpy and entropy will be done in the following analysis on energy consumption.

### 3. Impurity impacts on purification process

With the understanding of impurity impacts on the thermodynamic properties of CO<sub>2</sub>-streams, we analyzed impurity impacts on purification process by simulating compression, condensation and non-condensable gas separation theoretically.

#### 3.1. Impacts on the compression

Generally compression can be achieved in a number of ways, like undergoing an isothermal path, a polytropic path or an isotropic path. If we ignore the changes of kinetic energy and potential energy, the theoretical compression work required for a reversible steady flow process can be calculated by

$$w = \int v dP \quad (5)$$

where  $w$  is the compression work,  $v$  is volume, and  $P$  is pressure.

Theoretically the work required to compress a gas reversibly from a state to a final pressure is reduced as the compression path approaches the isothermal from the isotropic. However in an actual compression process, the isothermal compression is difficult to be realized and consequently it is a polytropic process. Due to the diversification of polytropic compression, the impurity impacts on isothermal compression and isentropic compression can only be studied instead. The results will give some insights regarding the impacts on polytropic compression.

With equations of state (EOS), the required work for an isothermal compression can be easily calculated from Eq. (5). For gas compression applications, the most frequently used equations of state are cubic EOSs, which include Redlich–Kwong, Peng–Robinson and Soave–Redlich–Kwong, Benedict–Webb–Rubin, Benedict–Webb–Rubin–Starling and Lee–Kessler–Ploeker [22]. It should be noted that the cubic equations are the most effective ways from a computational point of view, because the solution is found directly rather than through an iteration. In this study Peng–Robinson [23] EOS is chosen, so the theoretical isothermal compression work and isentropic compression work is

$$w_T = (P_2 v_2 - P_1 v_1) + RT \ln \left( \frac{v_1 - b}{v_2 - b} \right) + \frac{\sqrt{2}a}{2b} \coth \left( \frac{\sqrt{2}(-2v_2 - 2b)}{4b} \right) - \frac{\sqrt{2}a}{2b} \coth \left( \frac{\sqrt{2}(-2v_1 - 2b)}{4b} \right) \quad (6)$$

$$w_s = \int_{T_1}^{T_2} \sum y_i c_{p,i}^0 dT + h(T_1, P_1) - h(T_2, P_2) / \eta_{\text{isentropic}} \quad (7)$$

Some basic parameters related to the calculation are summarized in Table 3. In the calculations done in Section 3, only the mole fractions of one impurity and CO<sub>2</sub> were varied at the same time, while the mole fractions of other components were kept constant at the reference concentration.

Fig. 6 shows the isothermal compression work and the isentropic compression work at different compositions. Both the isothermal compression work and the isentropic compression work drop along with the increment of SO<sub>2</sub> and decrements of O<sub>2</sub>, N<sub>2</sub> and Ar,

almost linearly. Meanwhile comparatively the isothermal compression work is more sensitive to the change of SO<sub>2</sub>. When the mole fraction of SO<sub>2</sub> is changed by 1%,  $W_T$  is changed by 0.18 kW. However the isentropic compression work is more sensitive to the change of Ar. When the mole fraction of Ar is changed by 1%,  $W_s$  is changed by 0.36 kW.

Fig. 7 shows the discharging temperatures of isentropic compression of CO<sub>2</sub>-mixtures with the variations of different impurities. The increments of mole fractions of all impurities except SO<sub>2</sub> will result in a higher discharging temperature. Ar has more significant impacts than other non-condensable gases. Due to the high discharging temperature of isentropic compression, cooling

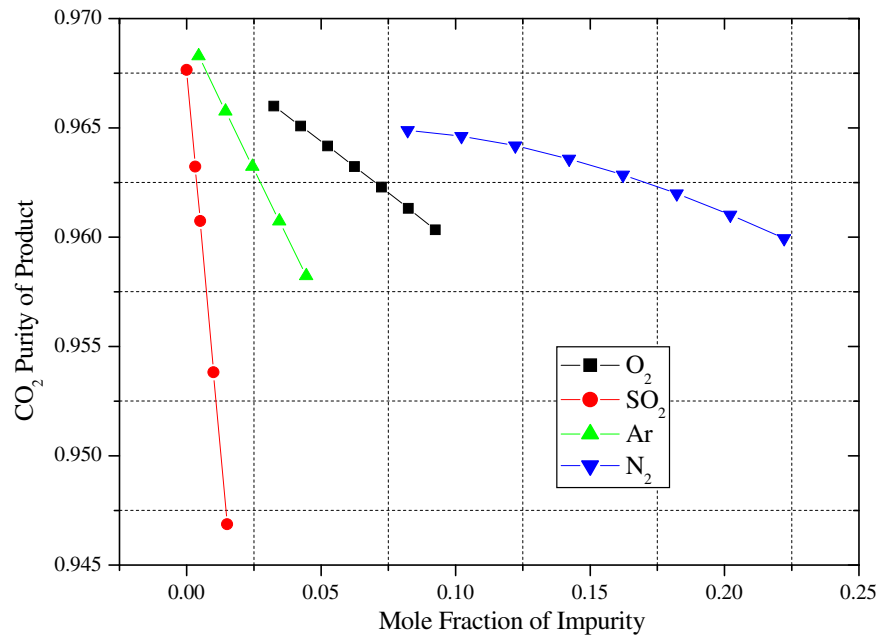


Fig. 10. Change of CO<sub>2</sub> purity of 2-stage-flash product with feed composition.

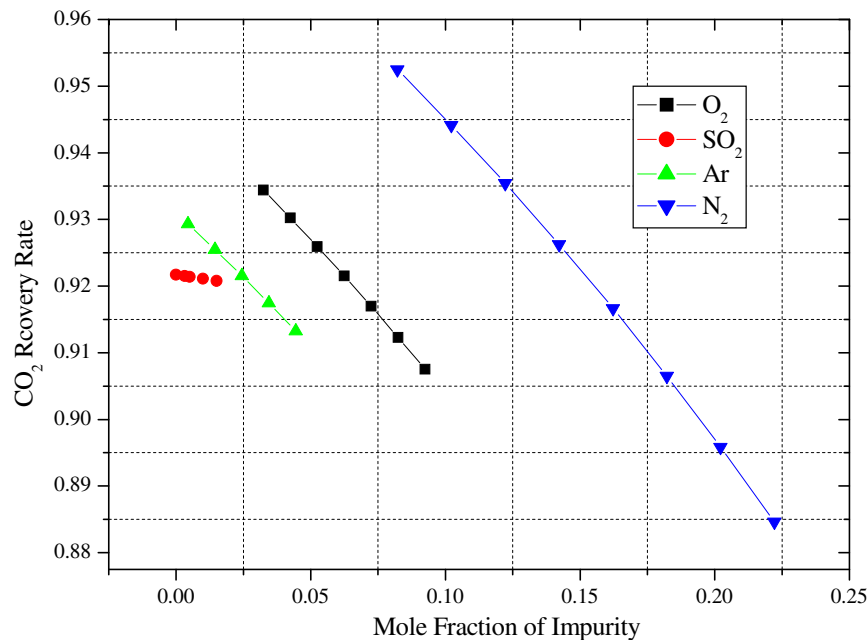


Fig. 11. Change of CRR of 2-stage-flash product with feed composition.



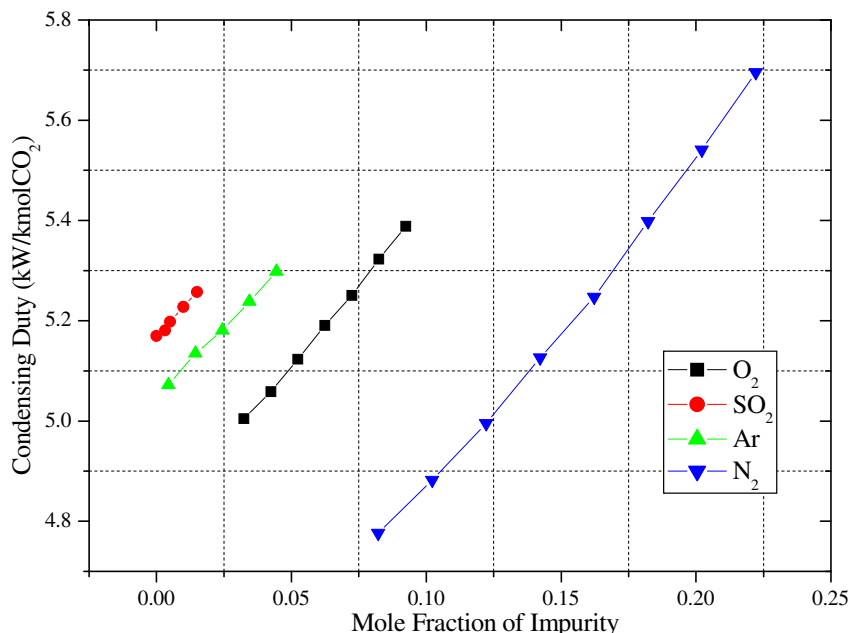


Fig. 12. Change of condensing duty of 2-stage-flash with feed composition.

is needed before CO<sub>2</sub>-stream is liquefied. Since the cooling duty is determined by the discharging temperature, the trends impurities affect the cooling duty (shown in Fig. 8) are similar to those on the discharging temperature (shown in Fig. 7). Because SO<sub>2</sub> has much larger heat capacities than other components, the cooling duty is more sensitive to the variations of SO<sub>2</sub>.

### 3.2. Impacts on non-condensable gas separation

The principle of physical separation is that to non-azeotropic mixtures, the composition of a component in either liquid or gas phase can be increased or decreased by varying the temperature or pressure. Since all of CO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/O<sub>2</sub> and CO<sub>2</sub>/Ar are non-azeotropic, CO<sub>2</sub>-streams is able to be purified by such physical separation methods, like flash or distillation.

#### 3.2.1. Flash system

Fig. 9 shows the process flow-sheet diagram of a 2-stage-flash system. The compressed CO<sub>2</sub>-stream, FEED, first passes through Condenser 1 where it is cooled and partially condensed, then the liquid and vapor phases are separated in Flash 1; since the vapor from Flash 1, Stream 3, still contains a large proportion of CO<sub>2</sub>, it goes into Condenser 2, being further cooled and partially condensed; and then Stream 5 is separated in Flash 2. The process is simulated by an in-house computer program. Some basic parameters related to the calculation are summarized in Table 4.

Figs. 10 and 11 show the changes of the CO<sub>2</sub> purity and CRR of the 2-stage-flash separation with feed compositions. Under the same operating conditions, the CO<sub>2</sub> purity of the purification product decreases when the mole fractions of impurities in FEED increase. SO<sub>2</sub> results in more influences than by others. For example, when the mole fraction of impurity is increased by 1%, the CO<sub>2</sub> purity of product is decreased by 1.38% by SO<sub>2</sub>, 0.25% by Ar, 0.09% by O<sub>2</sub> and 0.03% by N<sub>2</sub>, respectively. As to CRR, it also decreases when the mole fractions of impurities in FEED increase.

Due to the low condensing temperature, refrigeration is required, which means high energy consumption. Theoretical condensation duty is the sum of the enthalpy changes in Condenser 1 and Condenser 2. Because the flow rates of purification products

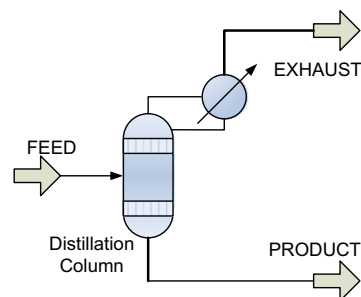


Fig. 13. Process flow-sheet diagram of distillation system.

Table 5

Parameters of distillation system

Parameters	Value
Flow rate	600 kg/h
Temperature of FEED	293.15 K
Operating pressure	3 MPa
Number of plates	5
CRR	92.15%
Reference composition of FEED (%mol)	
CO <sub>2</sub>	76%
O <sub>2</sub>	6% (±3%)
N <sub>2</sub>	15% (±7%)
Ar	2.5% (±2%)
SO <sub>2</sub>	0.5% (0–1.5%)

are varying with the compositions of FEED and operating conditions, it is more meaning to study the condensing duty recovering 1 kmol CO<sub>2</sub>, instead of the total condensing duty. The results are shown in Fig. 12. Generally the condensing duty rises almost linearly along with the increments of mole fraction of impurities; and if the mole fraction of impurity rises by 1%, averagely the condensing duty is increased by 0.059 kW/kmolCO<sub>2</sub> by SO<sub>2</sub>, 0.057 kW/kmolCO<sub>2</sub> by Ar, 0.064 kW/kmolCO<sub>2</sub> by O<sub>2</sub> and 0.066 kW/kmolCO<sub>2</sub> by N<sub>2</sub>. It verifies the conclusion given above that condensation may cost more energy if more N<sub>2</sub> is included.

### 3.2.2. Distillation column

Fig. 13 shows the process flow-sheet diagram of distillation system.  $\text{CO}_2$ -stream is fed in the middle of column and condensed partly at the top. When the liquid  $\text{CO}_2$ -mixture flows downward, it is heated by fed  $\text{CO}_2$ -stream and non-condensable gases are separated. The simulations on distillation are carried out in Aspen Plus. Some basic parameters related to the calculation are summarized in Table 5. Here the CRR of distillation is set as 92.15%, which is got by running 2-stage-flash at the reference composition of FEED.

From Fig. 14 it is easy to see that the increments of impurity mole fraction decrease the  $\text{CO}_2$  purity of distillation product, and the increment of  $\text{SO}_2$  has much more important impacts than other

impurities. Fig. 15 shows the change of the distillation condensing duty with feed compositions. If the mole fraction of impurity rises by 1%, averagely the condensing duty recovering 1 kmol  $\text{CO}_2$  is increased by 0.088 kW by  $\text{SO}_2$ , 0.030 kW by Ar, 0.031 kW by  $\text{O}_2$  and 0.032 kW by  $\text{N}_2$ .

We compared the performances of the 2-stage-flash system and the distillation column in Fig. 16. Results show that running at the same CRR and TPX conditions of FEED, the distillation column requires less energy, about 21% less, than the 2-stage-flash system. In addition the distillation column can produce a stream with higher  $\text{CO}_2$  purity than the 2-stage-flash system, which is important to reduce the volume to be transported and benefit the transportation process.

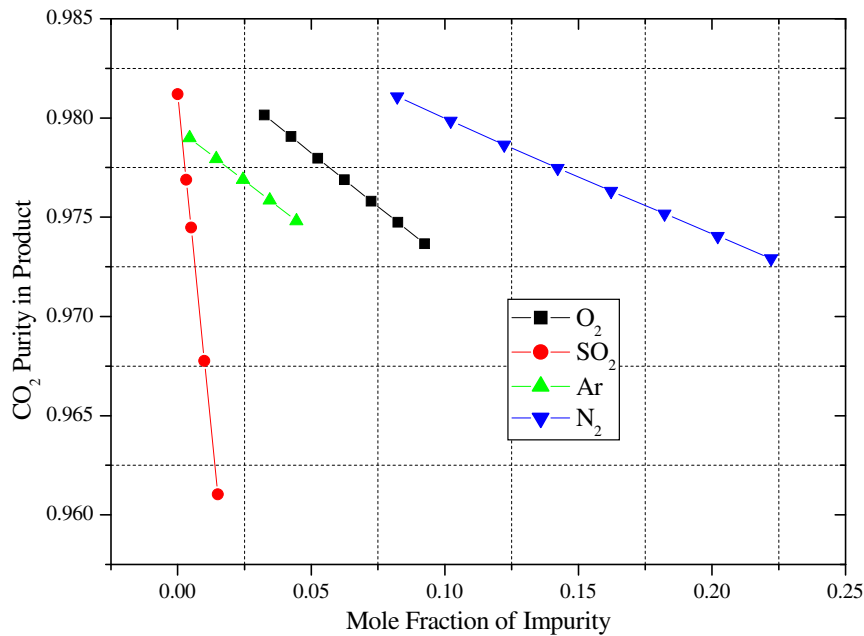


Fig. 14. Change of  $\text{CO}_2$  purity of distillation product with feed composition.

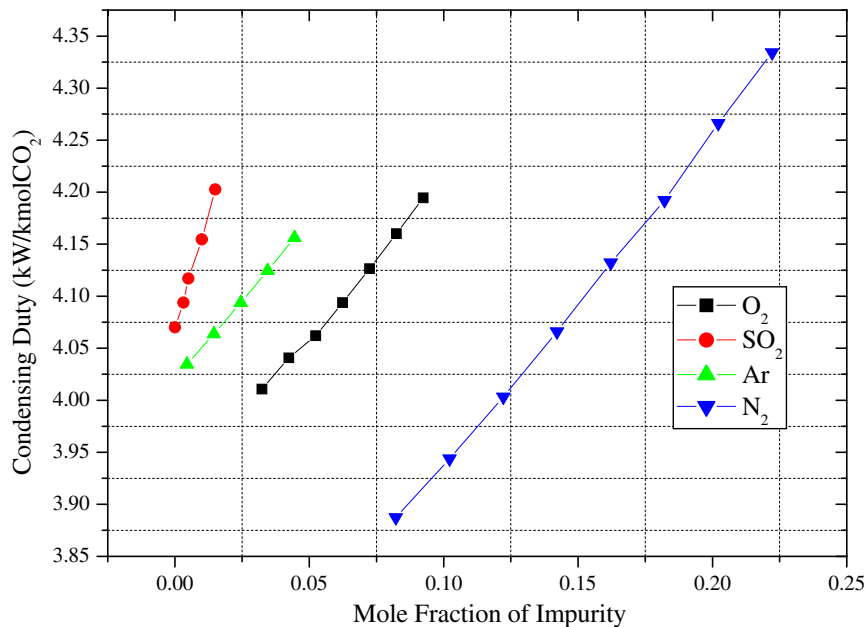


Fig. 15. Change of condensing duty of distillation with feed compositions.

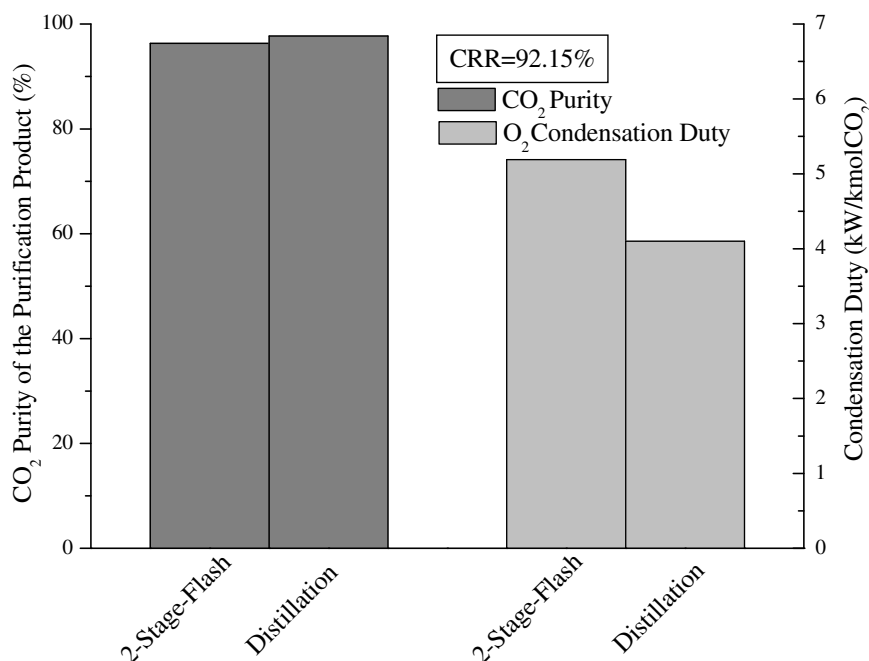


Fig. 16. Performance comparison between 2-stage-flash and distillation column.

#### 4. Discussions

For an optimum purification process in CCS, we desire stable operation, low energy consumption, simple configurations and high CO<sub>2</sub> purity in product, when CRR is kept consistent.

From the view point of stable operation: in general the concentration variations of all components may vary the purification process in all aspects, but in different degrees. Comparatively the non-condensable gases have quite similar impacts on the condensing conditions, SO<sub>2</sub> has more severe impacts on the CO<sub>2</sub> purity of product, and Ar has more obvious impacts on compression work. In order to stabilize the operation, the fraction fluctuations of impurities must be avoided, especially those of SO<sub>2</sub> and Ar.

From the view point of energy consumption, firstly because the increments of non-condensable gases may increase both compression work and the condensation duty of separation, the air leakage and excess oxygen in combustion should be controlled in a low level, secondly it should make the actual compression path approach the isothermal compression, which means that the compressors with good cooling or the multi-stage compression with intercooling are more desirable; and thirdly the distillation column is more preferable than flash systems.

From the view points of configuration and CO<sub>2</sub> purity of product, there is a conflict that simple configuration and high CO<sub>2</sub> purify cannot be achieved at the same time. Compared with the flash systems, the distillation columns have more complicated configurations, but are capable of producing CO<sub>2</sub>-streams with higher CO<sub>2</sub> purity.

#### 5. Conclusions and recommendations

Due to the existence of impurities, the thermodynamic properties of CO<sub>2</sub>-streams are changed clearly, and consequently the design and operation of purification process in the oxy-fuel combustion are significantly impacted. The conclusions can be drawn as follows:

- (1) The presence of non-condensable gases makes condensation more difficult and results in the increased pressure require-

ments for the condensation of the CO<sub>2</sub>-mixtures. Comparatively the operating conditions are more sensitive to the concentration variations of N<sub>2</sub> than those of O<sub>2</sub> and Ar.

- (2) Separating N<sub>2</sub> from CO<sub>2</sub> is much easier than separating O<sub>2</sub> and Ar. Under the same purification conditions, separating CO<sub>2</sub>/N<sub>2</sub> has a higher CO<sub>2</sub> purity in the product, compared with separating CO<sub>2</sub>/O<sub>2</sub> and CO<sub>2</sub>/Ar.
- (3) The presence of SO<sub>2</sub> results in higher heat capacities of CO<sub>2</sub>-mixtures while the presences of O<sub>2</sub>, Ar and N<sub>2</sub> give lower heat capacities of CO<sub>2</sub>-mixtures. Thus, the enthalpy and entropy of CO<sub>2</sub>-streams are increased with the increment of SO<sub>2</sub>, while decreased with the increment of O<sub>2</sub>, Ar and N<sub>2</sub>.
- (4) Comparatively the isothermal compression work is more sensitive to the concentration variations of SO<sub>2</sub>; while the isentropic compression work is more sensitive to the concentration variations of Ar. Moreover in order to save energy, it is much more desirable to compress CO<sub>2</sub>-mixtures containing non-condensable gases in the process which is close to isothermal compression.
- (5) Compared to flash column, distillation column requires less condensation duty. The energy saving is around 21% if CRR is 92.15%.

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#### References

- [1] Novak R, Lang G. Method for carbon dioxide recovery from a feed stream, Patent EP0964215; 1999.
- [2] Buhre BJP, Elliott LK, Sheng CD, Gupts RP, Wall TF. Oxy-fuel combustion technology for coal-fired power generation. *Prog Energ Combust Sci* 2005;31:283–307.
- [3] IPCC Special report on carbon dioxide capture and storage; 2005.
- [4] Heggum G, Weydahl T, Roald W, Mølnvik M, Austegard A. CO<sub>2</sub> conditioning and transportation, carbon dioxide capture for storage in deep geologic formations, vol. 2. Elsevier Inc.; 2005.
- [5] Kvamsdal HM, Jordal K, Bolland O. A quantitative comparison of gas turbine cycles with CO<sub>2</sub> capture. *Energy* 2007;32:10–24.

- [6] Yan J, Anheden M, Lindgren G, Stroberg L. Conceptual development of flue gas cleaning for CO<sub>2</sub> capture from coal-fired oxyfuel combustion power plant. In: Eighth international conference on greenhouse gas control technologies, June 19–22, Trondheim, Norway; 2006.
- [7] IEA Greenhouse Gas R&D Programme. Oxy combustion processes for CO<sub>2</sub> capture from power plants. Report No. 2005/09; 2005.
- [8] IEA Greenhouse Gas R&D Programme. Potential for improvement in gasification combined cycle power generation with capture of CO<sub>2</sub>. Report No. PH4/19; 2003.
- [9] IEA Greenhouse Gas R&D Programme. Improvement in power generation with post-combustion capture of CO<sub>2</sub>. Report No. PH4/33; 2004.
- [10] Oryshchyn D, Ochs T, Gerdemann S, Summers C, Patrick B. Developments in integrated pollutant removal for low-emission oxy-fuel combustion. In: Eighth international conference on greenhouse gas control technologies (GHGT-8), June, Trondheim, Norway; 2006.
- [11] White V, Allam R, Miller E. Purification of oxyfuel-derived CO<sub>2</sub> for sequestration or EOR. In: Eighth international conference on greenhouse gas control technologies (GHGT-8), June, Trondheim, Norway; 2006.
- [12] Li H, Yan J. Impact of impurities in CO<sub>2</sub>-fluids on CO<sub>2</sub> transport process. In: Proceedings of GT2006, ASME turbo expo 2006: power for land, sea and air, May 8–11, Barcelona, Spain; 2006.
- [13] Li H, Yan J. Preliminary study on CO<sub>2</sub> processing in CO<sub>2</sub> capture from oxy-fuel combustion. In: Proceedings of GT2007, ASME turbo expo 2007: power for land, sea and air, May 14–17, Montreal Canada; 2007.
- [14] Aspelund A, Jordal K. Gas conditioning – the interface between CO<sub>2</sub> capture and transport. *Int J Greenhouse Gas Control* 2007;1(3):343–54.
- [15] Li H, Ji X, Yan J. A new modification on RK EOS for gaseous CO<sub>2</sub> and gaseous mixtures of CO<sub>2</sub> and H<sub>2</sub>O. *Int J Energ Res* 2006;30(3): 135–48.
- [16] Li H, Yan J. Comparative study of equations of state (EOS) for CO<sub>2</sub> transportation in pipeline. In: Eighth international conference on greenhouse gas control technologies, June 19–22, Trondheim, Norway; 2006.
- [17] Li H, Yan J, Yan J, Anheden M. Evaluation of existing methods for the thermodynamic property calculation of CO<sub>2</sub>-mixtures. Vatterfall Report; 2007.
- [18] Holderbaum T, Gmehling J. PSRK a group contribution equation of state based on UNIFAC. *Fluid Phase Equilib* 1991;70:251–65.
- [19] Kunz O, Klimeck R, Wagner W, Jaeschke M. The GERG-2004 wide-range reference equation of state for natural gases. GERG technical monograph. Düsseldorf: Forsch.-Ber.VDI-Verlag; 2005.
- [20] McCabe WL, Smith JC. Unit operations of chemical engineering. McGraw-Hill Kogakusha Ltd.; 1976.
- [21] Perry RH, Green DW. Perry's chemical engineer's handbook. McGraw-Hill; 1997.
- [22] Mokhatab S, Poe WA, Speight JG. Handbook of natural gas transmission and processing. Elsevier Inc.; 2006.
- [23] Peng DY, Robinson DB. A new two-constant equation of state. *Ind Eng Chem Fundam* 1976;15:59–64.
- [24] Zanganeh KE, Shafeen A, Gupta M, Salvador C, Pearson B. Comparative performance evaluation of CO<sub>2</sub> compression and capture units for fossil fuel plants. In: Eighth international conference on greenhouse gas control technologies, June 19–22, Trondheim, Norway; 2006.