Integrated Master in Chemical Engineering

Steam and dry autothermal reforming of glycerol for H_2 production: Thermodynamic study including in situ CO_2 and/or H_2 separation

Master Thesis

by

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À Dokic e à Carlota.

Resumo

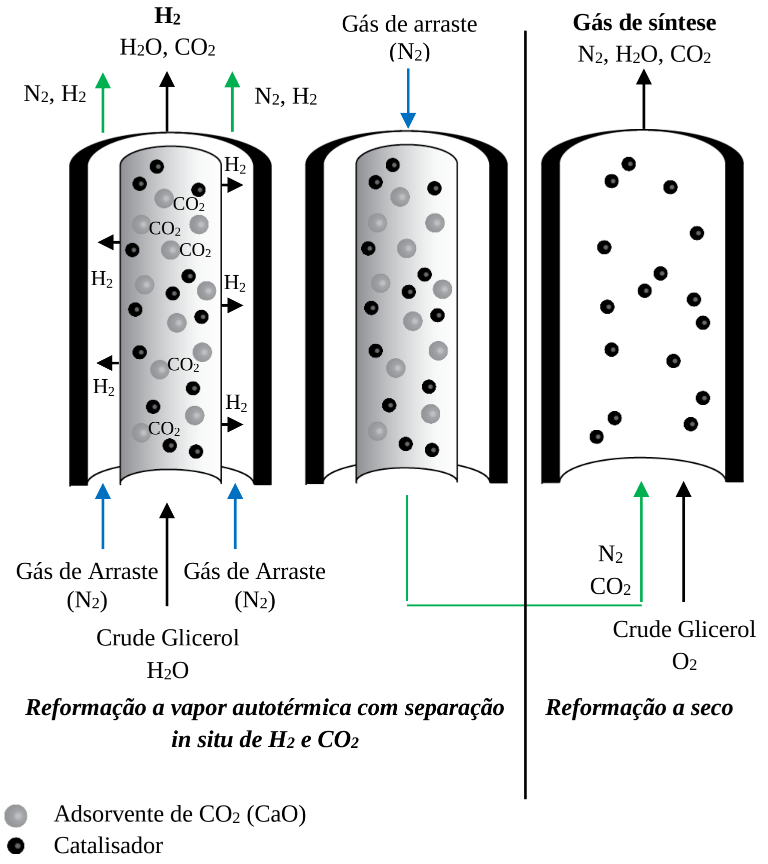
Nesta tese, a termodinâmica foi aplicada de forma a estudar os processos de reformação autotérmica a vapor e a seco de glicerol, que é um subproduto da produção de biodiesel, para produzir hidrogénio puro e gás de síntese, respetivamente. Os cálculos de equilíbrio foram realizados numa gama alargada de pressão (1-20 atm), temperatura (600-1000 K), razão molar oxigénio/glicerol na alimentação (0,0-3,0), razão molar dióxido de carbono/glicerol na alimentação (0,5-3,0) (apenas para a reformação a seco) e razão molar água/glicerol na alimentação (3-12) (apenas para a reformação a vapor). O efeito da separação *in situ* de CO_2 e H_2 é também investigado numa perspectiva de integração de processos de reação/separação num reator híbrido multifuncional (ver Resumo Gráfico). As composições de equilíbrio foram geradas com o *software* Aspen Plus® para um intervalo de razão molar adsorvente/glicerol entre 0 e 5 e fatores de separação de hidrogénio entre 0 e 0,99. Para além disso, foram encontradas as condições energeticamente neutras.

Os processos autotérmicos de reformação a vapor e a seco apresentam resultados semelhantes aos dos respectivos processos tradicionais (sem oxigénio na alimentação). No entanto, os rendimentos máximos de hidrogénio e gás de síntese decrescem com o teor de oxigénio na alimentação. Verificou-se, tal como já reportado para o processo tradicional, que a separação *in situ* de H_2 e de CO_2, no processo de reformação autotérmica a vapor, permite maximizar o rendimento de hidrogénio e eliminar completamente o metano, monóxido de carbono e dióxido de carbono. No caso do processo autotérmico a seco, mostrou-se que o mais adequado será operar sem separação de H_2 nem de CO_2, de modo a que haja uma utilização mais eficaz do CO_2 que é alimentado.

As condições ótimas e energeticamente neutras para o processo autotérmico a vapor foram encontradas quando tanto H_2 como CO_2 são separados do meio reacional, com um fator de separação de 0,8 e uma fraçao molar CaO/glicerol de 2,23. À pressão atmosférica, 900 K e a uma razão molar água/glicerol de 9 obteve-se um rendimento de hidrogénio de 6,93 (muito próximo do valor teórico de 7), não se mostrando necessária a adição de oxigénio à alimentação. As condições energeticamente neutras para o processo autotérmico a seco foram encontradas quando nem H_2 nem CO_2 são separados do meio reacional. À pressão atmosférica, 1000 K, a uma fraçao molar dióxido de carbono/glicerol de 1 e a uma razão molar oxigénio/glicerol de 0,75, obteve-se um rendimento de gás de síntese de 5,38 com uma razão molar H_2/CO de 1,12.

Palavras-Chave: Glicerol; Reformação; Autotérmica; Adsorção; Membrana;

Resumo Gráfico



Combinação dos processos autotérmicos de reformação a vapor e a seco: utilização do CO_2 produzido, adsorvido e posteriormente regenerado na reformação a vapor para produzir gás de síntese através da reformação a seco.

Abstract

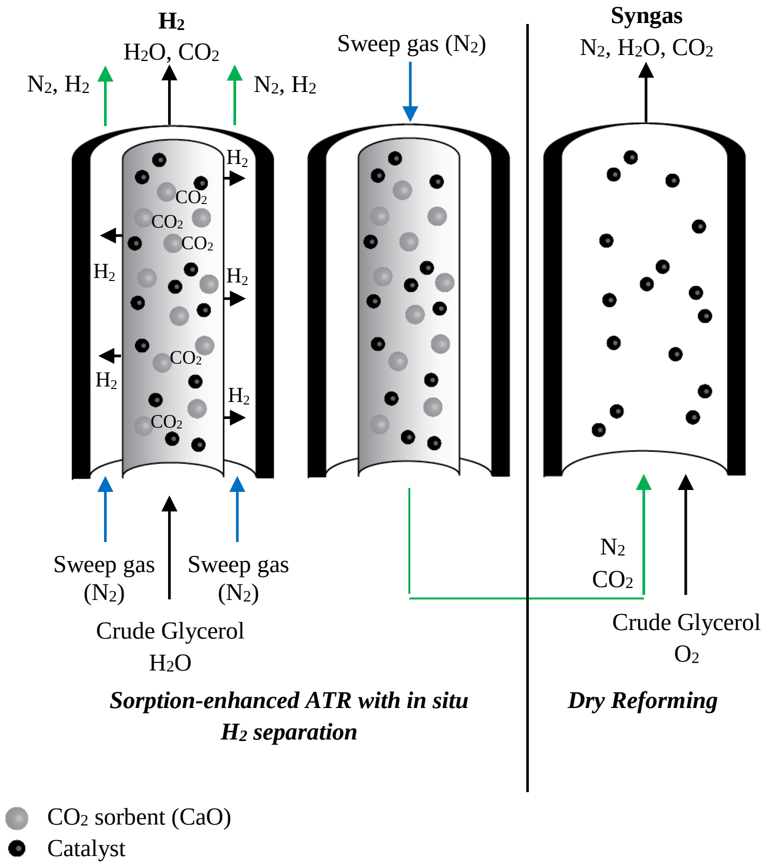
In this thesis, thermodynamics was applied to study the steam and dry autothermal reforming of glycerol, which is a by-product of biodiesel production, to generate pure hydrogen and syngas (H_2 and CO), respectively. Equilibrium calculations were performed in a wide range of pressure (1-20 atm), temperature (600-1000 K), oxygen to glycerol feed molar ratio (0.0-3.0), carbon dioxide to glycerol feed molar ratio (0.5-3.0) (only for dry autothermal reforming) and water to glycerol feed molar ratio (3-12) (only for steam autothermal reforming). The effect of CO_2 and/or H_2 in situ separation was investigated as well, in the perspective of reaction/separation process integration in a hybrid multifunctional reactor (cf. Graphical Abstract). The equilibrium compositions were generated with Aspen Plus® software for a sorbent to glycerol molar ratio range 0-5 and hydrogen separation factors in the range 0-0.99. Furthermore, the energetically neutral conditions were found.

The steam and dry autothermal reforming (ATR and DATR) processes present similar results compared to the traditional ones (with no oxygen in the feed). However, the maximum yields of hydrogen and synthesis gas decrease with the oxygen content in the feed. As reported for the steam reforming process (SR), the in situ separation of H_2 and CO_2 in ATR process maximizes the hydrogen yield and completely eliminates methane, carbon monoxide and carbon dioxide. Regarding DATR, the most adequate condition is the one where neither H_2 nor CO_2 is separated from the reaction medium, in order to efficiently use the CO_2 fed.

The optimal energetically neutral conditions for the ATR process were found when H_2 and CO_2 are removed in situ from the reaction medium with a H_2 separation factor of 0.8, a CaO/Glycerol ratio of 2.23 and no oxygen in the feed. Oxygen is not necessary to achieve energetically neutral conditions in the sorption-enhanced process due to the exothermicity of CO_2 sorption reactions. At atmospheric pressure, 900 K and water to glycerol feed molar ratio of 9, it was obtained a hydrogen yield of 6.93 (very close to the theoretical maximum value of 7). The optimal energetically neutral conditions for DATR process were found when neither H_2 nor CO_2 are removed in situ from the reaction medium. At atmospheric pressure, 1000 K, carbon dioxide to glycerol feed molar ratio of 1 and oxygen to glycerol feed molar ratio of 0.75, it was obtained a syngas yield of 5.38 with a H_2/CO ratio of 1.12.

Keywords: Glycerol; Reforming; Autothermal; Sorption-Enhanced; Membrane;

Graphical Abstract



Combination of steam and dry autothermal reforming processes: utilization of the CO_2 that is produced, adsorbed and subsequently regenerated in ATR to produce syngas via DATR.

Declaração

Ana Catarina Lacerda Leal declara, sob compromisso de honra, que este trabalho é original e que todas as contribuições não originais foram devidamente referenciadas com identificação da fonte.

Porto, 6 de Julho de 2015

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Notations

Latin and greek symbols

Formula Symbol	Unit	Definition
a	[-]	Number of atoms in the specie
b	[-]	Number of atoms in the feed
f	[-]	Separation factor
n	[kmol]	Number of moles
m	[kmol/h]	Molar flow rate
y	[-]	Mole fraction
G	[kJ/mol]	Gibbs free energy
ΔG_f	[kJ/mol]	Gibbs free energy of formation
P	[atm]	Pressure
$P_{\mathrm{H_2O}}^{sat}$	[atm]	Saturation vapor pressure
R	[J/(kmol K)]	Ideal gas universal constant
S	[J/K]	Entropy
T	[K]	Temperature
V	[m^3]	Volume
$\Delta H_{\mathrm{r}}^{298\ \mathrm{K}}$	[kJ/mol]	Standard enthalpy of reaction
Λ	[-]	Lagrangian multiplier
μ	[J/mol]	Chemical potential
$\hat{f}$	[atm]	Fugacity
$\hat{\phi}$	[-]	Fugacity coefficient

Indices

Index	Definition
$(\ )^0$	Standard conditions
$(\ )_i$	Chemical specie *i*
$(\ )_j$	Atom *j*

Abbreviations

Abbreviation	Definition
APR	Aqueous Phase Reforming
ATR	Autothermal Reforming
CCGFR	Carbon dioxide to Crude Glycerol Feed Ratio
CGFR	Carbon dioxide to Glycerol Ratio
CNF	Carbon Nanofiber
DATR	Dry Autothermal Reforming
DR	Dry Reforming
MSR	Methane Steam Reforming
OCGFR	Oxygen to Crude Glycerol Feed Ratio
OGFR	Oxygen to Glycerol Feed Ratio
PO	Partial Oxidation
RWGS	Reverse Water-Gas Shift
SCW	Super Critical Water
SR	Steam Reforming
WCGFR	Water to Crude Glycerol Feed Ratio
WGFR	Water to Glycerol Feed Ratio
WGS	Water-Gas Shift

Chemical Abbreviations

Molecular Formula	Name
Ag	Silver
Al_2O_3	Aluminum Oxide
C	Carbon (coke)
$CaCO_3$	Calcium Carbonate
CaO	Calcium Oxide
$Ca(OH)_2$	Calcium Hydroxide
C_nH_{2n+2}	Hydrocarbon
$C_3H_8O_3$	Glycerol
CH_3OH	Methanol
CH_4	Methane
Co	Cobalt
CO	Carbon Monoxide
CO_2	Carbon Dioxide
H_2	Hydrogen
H_2O	Water
MgO	Magnesium Oxide
N_2	Nitrogen
NaOH	Sodium Hydroxide
$NaCO_3$	Sodium Carbonate
O_2	Oxygen
Ru	Ruthenium
Pd	Palladium

CHAPTER I – Introduction

The fossil fuel depletion, together with the growing environmental concerns associated with fossil fuel utilization, has led to an increase on bio-based fuels demand. Biofuels are a feasible alternative solution because they are renewable and carbon dioxide neutral [1]. Consequently, their production has faced an extensive increase during the last decade, as depicted in Figure 1.1 for the particular case of biodiesel.

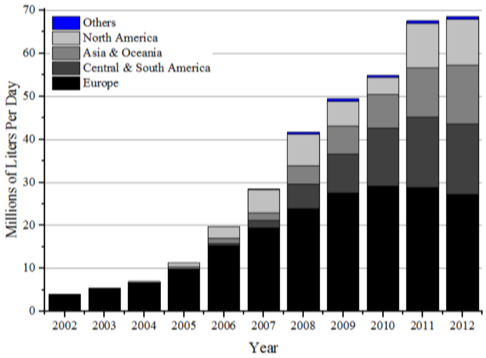

Figure 1.1. Worldwide biodiesel production between 2002 and 2012 [2].

Glycerol (1,2,3-propanetriol or glycerine), which is a by-product of biodiesel production by transesterification of vegetable oils (triglycerides) and methanol (Figure 1.2), is an industrial chemical with a multitude of applications in pharmaceutical, cosmetics and food industries (Figure 1.3). Glycerol represents ca. 10 wt. % of the final biodiesel product [3]. It is a low toxic alcohol, edible, biodegradable, non-flammable and with a high boiling point at atmospheric pressure (T_b = 290 ºC). Crude glycerol consists of glycerol, water, organic and inorganic salts, soap, methanol and traces of glycerides. Therefore, crude glycerol has a low commercial value as its low purity limits its application as industrial feedstock, whereas further refining is expensive [4]. However, glycerol utilization can have a great impact on the economics and sustainability of biodiesel production. So, the development of novel processes to convert crude glycol in other value-added products is being thoroughly investigated. Glycerol conversion into hydrogen (H_2) by its reforming is one of the possible routes [5].

Glycerol is a candidate source of hydrogen (H_2) that is renewable. Nowadays, still 95 % of hydrogen world’s production uses fossil fuels as raw material [1], namely via methane steam reforming (MSR). Here the steam reacts with methane as depicted in equation (1.1) [6].

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2,\ \Delta H_r^{298\ K} = 165\ kJ/mol \tag{1.1}$$

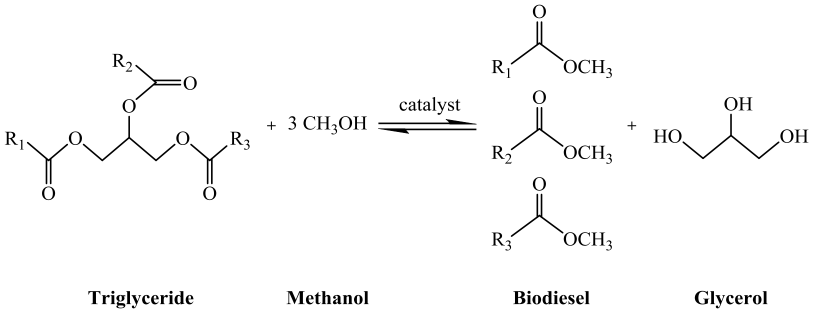

Figure 1.2. Transesterification of triglycerides to produce biodiesel.

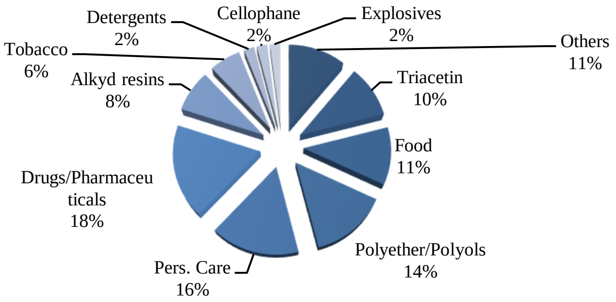

Figure 1.3. Glycerol applications and volumes (in percentage) [4].

By the stoichiometry, four moles of hydrogen are produced per each mole of methane consumed in MSR. On the other hand, the moles obtained by steam reforming of glycerol are seven, as per equation (1.2). Consequently, glycerol can be preferred as raw material for hydrogen synthesis once it can produce more moles of hydrogen than methane does. Moreover, the reaction is less endothermic, and makes use of a “waste”.

$$C_3H_8O_3 + 3H_2O \rightleftharpoons 7H_2 + 3CO_2,\ \Delta H_r^{298\ K} = 123\ kJ/mol \qquad (1.2)$$

The demand for H_2 has been increasing due to the technological advancements in fuel cells and the implementation of technologies with lesser effects to the environment, which is absolutely imperative. Hydrogen is seen as a free carbon energy carrier, so that from the combustion of H_2 with oxygen only results steam, as represented in equation (1.3). Although water vapour has a great impact on natural greenhouse effect, its atmospheric concentration is rather stable due to the natural hydrological cycle.

$$H_2 + 1/2O_2 \rightleftharpoons H_2O,\ \Delta H_r^{298\ K} = -286\ kJ/mol \qquad (1.3)$$

Hydrogen can be produced from glycerol via different processes [1]: steam reforming (SR), dry reforming (DR), partial oxidation (PO), autothermal reforming (ATR), dry autothermal reforming

(DATR), aqueous-phase reforming (APR) or super critical water (SCW) reforming. In this thesis, particular attention will be devoted to glycerol ATR and DATR.

1.1 Thesis outline

The dissertation is organized as follows:

In Chapter 2 a description of the existing processes for hydrogen production from glycerol is presented and the optimal conditions found by different authors are reported.

In chapter 3 it is explained the thermodynamic principle from which the equilibrium compositions were calculated and how this principle is applied in Aspen Plus® software. Moreover, the main assumptions made are stated.

In chapter 4, the results obtained from simulations are presented as along with the discussion.

In chapter 5 the conclusions and outlook for this dissertation are presented.

CHAPTER II – Literature Review

The reforming process, which is the preferred method for industrial scale hydrogen production, can be subdivided in two different reactions: the hydrocarbon splitting in the presence of water and the water gas shift (WGS) reaction, represented by equations (2.1) and (2.2), respectively.

$$C_nH_{2n+2} + nH_2O \rightleftharpoons nCO + (2n+1)H_2, \Delta H_r^{298\ \mathrm{K}} > 0 \tag{2.1}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2, \Delta H_r^{298\ \mathrm{K}} = -41\ \mathrm{kJ/mol} \tag{2.2}$$

The heat released by the WGS reaction is not sufficient to overcome the heat that is necessary for the splitting reaction of hydrocarbons, which is a highly endothermic reaction. Thus, the steam reforming process is endothermic.

There are numerous factors that thermodynamically affect the hydrogen production processes, which are the reaction temperature, total pressure, water to glycerol feed ratio (WGFR), oxygen to glycerol feed ratio (OGFR), carbon dioxide to glycerol feed ratio (CGFR) and feed reactants to inert gas ratio. These factors play a key role in order to reach high hydrogen yields. In the following sections is provided an overview of the main processes for hydrogen production from glycerol, as well as recommended operation conditions, from the thermodynamic point of view.

2.1. Hydrogen production processes from glycerol

In the different glycerol reforming processes, there is a group of reactions that may occur depending on the species that are present in the system. In most studies it was considered that $C_3H_8O_3$, H_2, H_2O, CO, CO_2, CH_4, C and O_2 (only for the ATR and PO process) are the existing compounds in the system and the possible reactions involved in each process are depicted in Table 2.1. The standard enthalpy of reactions presented in Table 2.1 were calculated using the parameters available in Aspen Plus ® V8.6 software.

2.1.1. Steam reforming

In the steam reforming process, which is a widely used method for producing hydrogen, the substrate is reacted with steam in the presence of a catalyst to produce hydrogen and carbon oxides. The overall process is endothermic and can be depicted by equation 2.3 (in Table 2.1).

Thermodynamically, the steam reforming process is favoured by high temperatures, low pressures and excess of steam [1]. The main concerns associated to this process are by-products formation (e.g., CO, CH_4, and coke), catalyst deactivation and high energy consumption [1].

Adhikari et al. [7] performed a thermodynamic analysis of this process, which revealed that the best conditions for producing hydrogen are temperatures > 900K, atmospheric pressure and water to glycerol molar ratio of 9:1. Under these conditions, the upper limit of hydrogen yield they have reached, which is defined as the moles of hydrogen produced per mole of glycerol fed, is 6. Furthermore, methane production is minimized and solid carbon formation is thermodynamically inhibited.

Table 2.1. Reactions considered during the simulations for the different reforming processes.

Reaction	$\Delta H_r^{298\ K}$ (kJ mol^{-1})	No.	Process
Steam Reforming			
$C_3H_8O_3 + 3H_2O \rightleftharpoons 7H_2 + 3CO_2$	123	(2.3)	SR, ATR
Decomposition of glycerol			
$C_3H_8O_3 \rightleftharpoons 3CO + 4H_2$	246	(2.4)	SR, ATR, DR, PO, DATR
Water-gas shift			
$CO + H_2O \rightleftharpoons H_2 + CO_2$	-41	(2.5)	SR, ATR, DR, PO, DATR
Methanation			
$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$	-206	(2.6)	SR, ATR, DR, PO, DATR
Steam reforming of methane			
$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2$	165	(2.7)	SR, ATR, DR, PO, DATR
Dry reforming of methane			
$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$	247	(2.8)	SR, ATR, DR, PO, DATR
Carbon formation			
$2CO \rightleftharpoons CO_2 + C$	-172	(2.9)	SR, ATR, DR, PO, DATR
$CH_4 \rightleftharpoons 2H_2 + C$	74	(2.10)	SR, ATR, DR, PO, DATR
$CO + H_2 \rightleftharpoons H_2O + C$	-131	(2.11)	SR, ATR, DR, PO, DATR
$CO_2 + 2H_2 \rightleftharpoons 2H_2O + C$	-90	(2.12)	SR, ATR, DR, PO, DATR
Glycerol Oxidation			
$C_3H_8O_3 + 1/2O_2 \rightleftharpoons 2CO + CO_2 + 4H_2$	-37	(2.13)	ATR, PO, DATR
$C_3H_8O_3 + O_2 \rightleftharpoons CO + 2CO_2 + 4H_2$	-319	(2.14)	ATR, PO, DATR
$C_3H_8O_3 + 3/2O_2 \rightleftharpoons 3CO_2 + 4H_2$	-602	(2.15)	ATR, PO, DATR
$C_3H_8O_3 + 7/2O_2 \rightleftharpoons 3CO_2 + 4H_2O$	-1569	(2.16)	ATR, PO, DATR
Carbon monoxide oxidation			
$CO + 1/2O_2 \rightleftharpoons CO_2$	-283	(2.17)	ATR, PO, DATR
Methane Oxidation			
$CH_4 + 1/2O_2 \rightleftharpoons CO + 2H_2$	-36	(2.18)	ATR, PO, DATR
$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O$	-802	(2.19)	ATR, PO, DATR
Carbon Oxidation			
$C + 1/2O_2 \rightleftharpoons CO$	-110	(2.20)	ATR, PO, DATR
$C + O_2 \rightleftharpoons CO_2$	-393	(2.21)	ATR, PO, DATR

2.1.2. Dry reforming

In the dry reforming process the substrate is fed to the reactor with carbon dioxide in the absence of steam. Except for the overall steam reforming reaction (equation 2.3), which is the sum of the decomposition of glycerol and three times the WGS reaction, the possible reactions involved in dry and steam reforming processes are the same. The difference between them lies in the reactions that are more favoured in each case. The main advantage of this technology is the possibility of converting CO_2, which is a greenhouse gas, by the reverse of WGS reaction. Moreover, CO_2 may be converted into value-added inert carbon, such as carbon nanofiber (CNF), if suitable catalysts are used, being sequestered and removed from the carbon biosphere cycle [8].

Nevertheless, the formation of carbon monoxide increases with the carbon dioxide to glycerol feed ratio (CGFR), which leads to a limitation on the application of hydrogen in fuel cells. However, it is a good opportunity to produce syngas (mixture of CO and H_2) for other applications (e.g. Fischer–Tropsch process). According to Wang et al [8], who performed a thermodynamic analysis, the optimum conditions for syngas production are 1000 K, atmospheric pressure and carbon dioxide to glycerol molar ratio of 1, at which 6.4 mole of synthesis gas (H_2/CO molar ratio = 1) is produced per mole of glycerol fed with CO_2 conversion of 33 %.

2.1.3. Partial oxidation

In the partial oxidation (PO) process, part of the substrate is reacted with oxygen at sub-stoichiometric ratios. The glycerol oxidation is an exothermic reaction that provides the required heat for the reforming reaction internally [1]. Equations 2.13 to 2.16 depict the possible glycerol oxidation reactions whereas equation 2.17 represents the carbon monoxide oxidation reaction. Equations 2.18 and 2.19 show the methane oxidation reactions and finally equations 2.20 and 2.21 depict the carbon oxidation reactions.

The oxidation step of the process can be conducted in the presence or absence of a catalyst. The catalyst determines de relative extents of the oxidation and reforming reactions [9]. The oxygen to glycerol feed ratio (OGFR) has an impact on glycerol conversion and hydrogen selectivity. Experimentally [1], it was observed that hydrogen selectivity decreases with the OGFR (more oxygen) until a certain value from which it starts to increase due to the temperature increase. The temperature decrease also results in lower glycerol conversion [1].

Wang [10] performed a thermodynamic analysis of the PO process for hydrogen production from glycerol, which showed that the optimum conditions to obtain the maximum hydrogen formation are temperatures between 1000 and 1100 K and oxygen to glycerol molar ratios of 0.4-0.6 at 1 atm. Under these conditions, it was achieved a complete conversion of glycerol, absence of solid carbon and hydrogen and carbon monoxide yields of 79.93 % - 87.31 % and 75 % - 87.97 %, respectively.

2.1.4. Autothermal reforming

The authothermal reforming is a combination of PO and SR processes where the substrate is reacted with both steam and oxygen. Thus, the steam reforming process “absorbs” the heat generated by the partial oxidation process.

Although the ATR process has energetic advantages over conventional SR, the H_2 that is produced in the latter is greater than that in the ATR [3]. Wang et al. [11] did a thermodynamic analysis of autothermal reforming and reported that temperatures of 900 – 1000 K, steam to glycerol ratios of 9-12 and oxygen to glycerol ratios of 0.0-0.4 are preferred for hydrogen production. To achieve conditions at which the heat duty of the reformer is zero (thermoneutral conditions) under the optimal temperature range, it is necessary an oxygen to glycerol feed ratio of around 0.36 at 900 K and 0.38-0.39 at 1000 K. At thermoneutral conditions, the maximum number of moles of hydrogen obtained per mole of glycerol fed is 5.63 (900 K and steam to glycerol ratio of 12).

2.1.5. Dry autothermal reforming

The dry authothermal reforming is a combination of PO and DR processes where the substrate is reacted with both carbon dioxide and oxygen. Thus, the partial oxidation reactions may generate the heat required by the reforming reaction.

Kale and Kulkarni [12] performed a thermodynamic analysis of dry autothermal reforming (DATR) of glycerol for the temperature range 600 – 1000 K, 1 bar pressure, OGFR 0.3 to 1.5 and CGFR 1 to 5. The results of their work show that higher values of OGFR and CGFR yielded a syngas ratio close to 1, which is desirable for use in petrochemical manufacture, with lower carbon and methane formation. On the other hand, lower values of OGFR and CGFR yielded more hydrogen with low steam and carbon dioxide production. The optimal condition for DATR of glycerol was observed at 926.31 K, 1 bar, OGFR = 0.9 and CGFR = 1 that gave 2.67 mol of hydrogen and 4.8 mol of syngas (H_2/CO molar ratio of 1.25) with negligible methane and carbon formations.

2.1.6. Aqueous-phase reforming and supercritical water reforming

The aqueous-phase reforming (APR) is a process that is operated at low temperatures (~540 K) and high pressures (~60 atm), the opposite conditions of the other technologies. The reactions that may occur in this process are the same as for the steam reforming process. The main advantage of APR is that it is a liquid phase process, thus it is not necessary to vaporize biomass-based liquids, which have high boiling points. Also, there is less CO production comparing to the other processes [1]. On the other hand, this process requires high pressure and has low H_2 selectivity (because methane formation, which is represented by equation 2.6 in Table 2.1, is favoured at low temperature) [3]. Seretis and Tsiakaras [13] did a thermodynamic study of hydrogen production via aqueous phase reforming of glycerol and found that the best conditions to optimize hydrogen production and minimize methane and carbon formation are pressure ratios $P/P_{\mathrm{H_2O}}^{\mathrm{sat}}$ between 1 and 1.2, temperatures between 450 and 550 K and WGFR between 9 and 14.

The supercritical water (SCW) reforming is a process that is performed under the critical temperature and pressure conditions. Supercritical water is water that is heated and compressed at 647 K and 221 bar (~218 atm), respectively. The main properties of SCW are its low dielectric constant and the lower number of hydrogen bonds compared with liquid water. As a result, organic compounds and even gases are soluble in SCW, which means that the reactions can be conducted in a single fluid phase. Moreover, there is high concentration of H^+ and OH^- ions in SCW, which allows it to act as an acid or base catalyst in the reactions. Thus, it is possible to operate the reforming process in the absence of a solid catalyst [14].

Ortiz et al [14] conducted a thermodynamic study of supercritical water reforming of glycerol, which revealed that the best conditions to optimize hydrogen production are 1173 K and 1 mol % glycerol in the feed. Under these conditions a hydrogen purity of about 95 % is achieved. However, it is recommended to operate at temperatures from 1023 to 1073 K in order to reduce the energy cost and extend the durability of materials. Furthermore, the operating pressure did not affect the results in the studied range (200 – 300 atm).

An experimental study [15] shows that glycerol is completely gasified to H_2, CO_2 and CH_4 and trace amounts of CO by reforming in supercritical water over Ru/Al_2O_3 catalysts. At dilute concentrations (5 wt. % glycerol in water), a H_2 yield of 6.5 mol H_2/ mol $C_3H_8O_3$ was obtained at 1073 K and 241 bar, which is close to the theoretical yield of 7 mol H_2/ mol $C_3H_8O_3$.

2.2. Possible solutions for the challenges in the glycerol reforming processes

2.2.1. Carbon dioxide removal

According to the Le Chatelier’s principle, carbon dioxide removal from the reaction zone results in an equilibrium shift of the reforming reaction to the side of hydrogen production (reducing also CH_4 and CO by-products). This can be done through in situ sorption-enhanced reforming, where the reactor is filled with a mixture of catalyst-adsorbent. The most common adsorbent reported in thermodynamic studies for the sorption of CO_2 upon glycerol reforming is calcium oxide (CaO) [6], which reacts with CO_2 to form calcium carbonate ($CaCO_3$). Alternatively, alkali (NaOH) can be added to the feed in order to react with CO_2 and yield sodium carbonate ($NaCO_3$) [6]. Magnesium oxide (MgO) based sorbents have also been studied as potential CO_2 sorbents but experimental results [16] showed that the reaction rates for this kind of sorbents are too slow, which limits their application to industrial scale. Moreover, the sorption capacity of these sorbents is far less than the calcium-based ones [16]. The reactions that describe the carbon dioxide sorption are represented in Table 2.2.

Table 2.2. Carbon dioxide sorption reactions considered during the simulations.

Reaction	$\Delta H_r^{298\ K}$ (kJ mol^{-1})	No.	Process
CO_2 Sorption			
$CaO + H_2O \rightleftharpoons Ca(OH)_2$	-109	(2.22)	SR, ATR
$Ca(OH)_2 + CO_2 \rightleftharpoons CaCO_3 + H_2O$	-70	(2.23)	SR, ATR

There are some researchers who already studied the influence of carbon dioxide removal in the glycerol steam reforming process [17, 18]. Chen et al. [17] performed a thermodynamic analysis on the sorption-enhanced steam reforming of glycerol for hydrogen production without considering a specific CO_2 adsorbent but specifying CO_2 separation factors. Their results show that CO_2 removal from the reaction medium enhances glycerol conversion to hydrogen as well as its maximum yield (moles of hydrogen produced per mole of glycerol fed), which can be increased from 6 to 7. The optimum conditions are temperatures between 800 and 850 K (about 100 K lower than that for steam reforming without CO_2 sorption), atmospheric pressure, and steam to glycerol molar feed ratio around 9. Furthermore, CO_2 sorption may suppress the carbon formation reaction. Li et al. [18] investigated the same process but, instead of setting the CO_2 separation factor, they studied the effect of CaO as adsorbent. The optimum operation conditions reported by the authors are 900 K, water to glycerol molar ratio of 4, atmospheric pressure and calcium oxide to glycerol molar ratio of 10 [18].

Although the effect of CO_2 sorption is only reported for the steam reforming of glycerol, this solution may also promote the reforming reactions for the other processes depicted in the previous section, except for the dry reforming process, which uses excess of CO_2 in order to convert it into syngas.

2.2.2. Hydrogen in situ separation

Instead of CO_2 sorption, in situ separation of hydrogen can also be an option to promote the reforming reaction and consequently increase the yield of hydrogen. In this case, a membrane reactor is needed in order to selectively separate hydrogen from the reaction medium.

Palladium-based membranes, which are extremely perm-selective for hydrogen, have been extensively studied and applied in pure hydrogen production processes [19]. These membranes offer low resistance to hydrogen transport, which occurs through the solution/diffusion mechanism. The commercialization of pure palladium membranes is limited due to the embrittlement phenomenon and their high cost. Instead, palladium alloys containing another metal, such as silver, are used. These alloys can improve not only the chemical resistance of the membrane but also the hydrogen permeability. An experimental study about glycerol steam reforming in a dense Pd-Ag membrane reactor showed that it is possible to achieve a hydrogen recovery above 60 % using Co/Al_2O_3 as catalyst at 673 K and 4 atm [19].

There are some thermodynamic studies in the literature about glycerol steam reforming with hydrogen removal [20, 21]. For the other processes, namely, autothermal and dry reforming, no publications were found. Wang et al. [21] studied the influence of in situ hydrogen separation on the glycerol steam reforming process. Their results suggest that 7 moles of hydrogen per mole of fed glycerol (maximum possible value) can be obtained even at 600 K due to the hydrogen removal, for separation factors above 0.99. The optimum conditions are water to glycerol feed ratio around 9 and temperatures between 825 and 875 K. Also, for a high fraction of H_2 removal, the influence of increasing pressure in terms of hydrogen production becomes marginal above 800 K.

2.2.3. In situ hydrogen and carbon dioxide simultaneous separation

The combination of hydrogen and carbon dioxide removal from the reaction medium may significantly improve hydrogen production. Silva et al. [20] reported recently that nearly 7 moles of hydrogen per mole of reacted glycerol (stoichiometric value) can be obtained at 700 K, WGFR of 9, atmospheric pressure and for separation factors of carbon dioxide and hydrogen of 0.99 and 0.80, respectively. This value represents and enhancement of 47 % and 22 % comparatively to the sorption-enhanced reactor ($f_{\mathrm{CO_2}}$= 0.99) and membrane reactor ($f_{\mathrm{H_2}}$= 0.80), respectively [20].

2.3. Pure vs Crude Glycerol

Few studies have been performed using crude glycerol as raw material for the reforming processes. The crude glycerol consists of water, non-converted methanol, ash and fatty materials. As previously stated in the introduction (chapter I), the purification of crude glycerol is highly expensive. Thus, if the refining stage could be eliminated, the overall cost of the glycerol reforming process would decrease. Authayanun et al. [22] did a thermodynamic study of hydrogen production from crude glycerol through autothermal reforming. Crude glycerol was assumed to be a mixture of glycerol and methanol and four different compositions were studied. The results showed that an increase in the ratio of glycerol to methanol in crude glycerol lead to an increase in the amount of hydrogen produced. This effect is observed because the glycerol steam reforming and oxidation reactions produce, per stoichiometry, a greater number of moles of hydrogen than the methanol decomposition and oxidation reactions, which are depicted in Table 2.3.

Table 2.3. Methanol reactions considered during the simulations.

Reaction	$\Delta H_{\mathrm{r}}^{298\ \mathrm{K}}$ (kJ mol^{-1})	No.	Process
Steam Reforming			
$CH_3OH + H_2O \rightleftharpoons 3H_2 + CO_2$	49	(2.24)	SR, ATR
Methanol Decomposition			
$CH_3OH \rightleftharpoons 2H_2 + CO$	90	(2.25)	SR, ATR, DR, PO, DATR
Methanol Oxidation			
$CH_3OH + 1/2O_2 \rightleftharpoons 2H_2 + CO_2$	-192	(2.26)	ATR, PO, DATR
$CH_3OH + 3/2O_2 \rightleftharpoons 2H_2O + CO_2$	-676	(2.27)	ATR, PO, DATR

2.4. Work purpose

The aim of this thesis is to more deeply understand the glycerol autothermal reforming process for hydrogen production as well as the role that each parameter, such as operating pressure, temperature and feed composition plays on its optimization. This work focuses on the ATR process because it is an attractive alternative, from an energetic point of view, to the extensively studied SR process. Besides, solutions such as in situ hydrogen removal, which may potentially improve the hydrogen yield, have not been studied for ATR process yet. To accomplish this objective, a thermodynamic study is performed to access the conditions at which hydrogen yield and purity are maximized, at the equilibrium.

Glycerol reforming is a highly endothermic reaction, which means that the process must operate at high temperatures and consequently with additional operational cost. The main challenge is to find if it is possible to eliminate the necessity of external heating supply, and yet without compromising the hydrogen yield. Different solutions (e.g. in situ hydrogen and carbon dioxide removal or introduction of O_2 into the reformer) are analysed in this thesis in order to discuss the pros and cons of implementing them and to try to identify the conditions that best meet these challenges.

This thesis also includes an investigation of the DATR process as an energetically more feasible alternative to the DR process. The effects of in situ hydrogen separation as well as of OCGFR on syngas production, carbon dioxide conversion and H_2/CO ratio are analysed.

Moreover, it is important to take into account that the glycerol resulting from biodiesel production is not in its pure state, but in a mixture with other compounds like unreacted methanol. So, the study is carried out for different crude compositions and their effects on hydrogen yield and purity are also addressed.

CHAPTER III – Methodology

In order to determine the equilibrium composition of the species in the system, a non-stoichiometric approach, which involves the minimization of the Gibbs free energy, was used. There are several advantages of using this method including the easy achievement of convergence in computation. Furthermore, no preset selection of possible chemical reactions or accurate estimation of initial equilibrium compositions are required [17].

The total Gibbs free energy (*G*) is dependent on temperature (*T*), pressure (*P*) and molar quantities of the *N* components in the system, and its differential form can be written as follows:

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \sum_{\mathrm{i}=1}^{\mathrm{N}} \mu_{\mathrm{i}}\mathrm{d}n_{\mathrm{i}} \tag{3.1}$$

where S is the entropy, V is the volume, n_i is the number of moles of component *i* in the system and μ_i is the chemical potential of component *i*. When the temperature and pressure of the system are constant, equation (3.1) becomes:

$$\mathrm{d}G = \sum_{\mathrm{i}=1}^{\mathrm{N}} \mu_{\mathrm{i}}\mathrm{d}n_{\mathrm{i}} \tag{3.2}$$

The Gibbs free energy reaches a minimum at equilibrium, which implies equation (3.2) is equal to zero. From equation (3.2) one can write the total Gibbs free energy as:

$$G = \sum_{\mathrm{i}=1}^{\mathrm{N}} \mu_{\mathrm{i}}n_{\mathrm{i}} = \sum_{\mathrm{i}=1}^{\mathrm{N}} n_{\mathrm{i}}G_{\mathrm{i}}^{0} + RT\sum_{\mathrm{i}=1}^{\mathrm{N}} n_{\mathrm{i}}\ln\left(\frac{\hat{f}_{\mathrm{i}}}{f_{\mathrm{i}}^{0}}\right) \tag{3.3}$$

where G_{i}^{0}, $\hat{f}_{\mathrm{i}}$, f_{i}^{0} are the standard Gibbs free energy, the fugacity and the standard-state fugacity of species *i* in the system, respectively. G_{i}^{0} is assumed to be zero for each chemical element in its standard state, thus $G_{\mathrm{i}}^{0} = \Delta G_{f_{\mathrm{i}}}^{0}$ is assumed. Moreover, for reaction equilibria in gas phase, $\hat{f}_{\mathrm{i}} = \hat{\phi}_{\mathrm{i}}y_{\mathrm{i}}P$ and $f_{\mathrm{i}}^{0} = P^{0}$, where y_{i} is the mole fraction of component *i*, *P* and P^0 are the pressure of the system and the standard-state pressure of 1 atm, respectively, and $\hat{\phi}_{\mathrm{i}}$ is the fugacity coefficient of the gas mixture, which can be calculated using the Soave-Redlich-Kwong equation of state (see appendix A) [23]. This property method is suitable for nonpolar or moderately polar mixtures (e.g. methane, hydrogen and carbon dioxide) and for processes with high operating temperature [20].

By introducing the constrains of elemental balances and the Lagrangian multipliers, λ_i, a new function *G´* can be written as follows:

$$\sum_{\mathrm{i}=1}^{\mathrm{N}} a_{\mathrm{ji}} n_{\mathrm{i}} = b_{\mathrm{j}}\,, \qquad \mathrm{j} = 1, \dots, \mathrm{M} \tag{3.4}$$

$$G' = \sum_{\mathrm{i}=1}^{\mathrm{N}} n_{\mathrm{i}} G_{\mathrm{i}}^{0} + RT \sum_{\mathrm{i}=1}^{\mathrm{N}} n_{\mathrm{i}} \ln\left(\frac{\hat{\phi}_{\mathrm{i}} y_{\mathrm{i}} P}{P^{0}}\right) + \sum_{\mathrm{j}=1}^{\mathrm{M}} \lambda_{\mathrm{i}} \left(\sum_{\mathrm{i}=1}^{\mathrm{N}} a_{\mathrm{ji}} n_{\mathrm{i}} - b_{\mathrm{j}}\right) \tag{3.5}$$

where a_{ji} is the number of atoms *j* in the species *i* and b_{j} is the total number of atoms *j* in the feed. The derivative of *G´* with respect to n_{i} must be zero in order to find the composition at its minimum value, which leads to the following equation:

$$\left(\frac{\delta G'}{\delta n_{\mathrm{i}}}\right)_{T,P,n_{\mathrm{j}\neq\mathrm{i}}} = \Delta G_{f_{\mathrm{i}}}^{0} + RT \ln\left(\frac{\hat{\phi}_{\mathrm{i}} y_{\mathrm{i}} P}{P^{0}}\right) + \sum_{\mathrm{j}=1}^{\mathrm{M}} \lambda_{\mathrm{i}} a_{\mathrm{ji}} = 0, \qquad i = 1, \dots, N \tag{3.6}$$

or

$$\Delta G_{f_{\mathrm{i}}}^{0}/RT + \ln\left(\frac{P}{P^{0}}\right) + \ln\left(\hat{\phi}_{\mathrm{i}}\right) + \ln\left(\frac{n_{\mathrm{i}}}{n_{\mathrm{T}}}\right) + \sum_{\mathrm{j}=1}^{\mathrm{M}} \lambda_{\mathrm{i}} a_{\mathrm{ji}} \Big/ RT = 0, \qquad i = 1, \dots, N \tag{3.7}$$

where n_{T} is the total number of moles of all species defined by:

$$n_{\mathrm{T}} = \sum_{\mathrm{i}=1}^{\mathrm{N}} n_{\mathrm{i}} \tag{3.8}$$

Equations (3.6), (3.7) and (3.8) represent a non-linear system of $M + N + 1$ equations that can be solved for the unknowns n_{i} and λ_{i} and y_{i} at equilibrium.

When solid-phase carbon (graphite) is considered, standard Gibbs energy of carbon, $G_{\mathrm{C(s)}}^{0}$, is assumed to be zero [23]. However, for a temperature-steady process

$$\mathrm{d}G_{\mathrm{C(s)}}(T,P) = V_{\mathrm{C}}\mathrm{d}P \tag{3.9}$$

V_{C}, which is the mole volume of solid carbon, can be considered as constant because it is less affected by temperature and pressure.

$$G_{\mathrm{C(s)}}(T,P) - G_{\mathrm{C(s)}}(T,P^{0}) = V_{\mathrm{C}}(P - P^{0}) \tag{3.10}$$

$$G_{\mathrm{C(s)}}(T,P) = V_{\mathrm{C}}(P - P^{0}) \tag{3.11}$$

Considering the presence of solid-phase carbon in the system, equation (3.7) becomes

$$\Delta G_{f_\mathrm{i}}^{0}/RT + \ln\left(\frac{P}{P^0}\right) + \ln(\hat{\phi}_\mathrm{i}) + \ln\left(\frac{n_\mathrm{i}}{n_\mathrm{T}}\right) + \sum_{\mathrm{j}=1}^{\mathrm{M}} \lambda_\mathrm{i} a_\mathrm{ji} \Big/ RT + n_\mathrm{C} G_{\mathrm{C(s)}}/RT = 0, \quad i = 1, \dots, N-1 \qquad (3.12)$$

The thermodynamic analysis of glycerol reforming processes was performed by using Aspen Plus® V8.6 software, aiming to study the effect of key operating parameters on hydrogen production. A GIBBS reactor, which is a simplified reactor model based on the Gibbs free energy minimization, was utilized to calculate the equilibrium compositions of the species assumed to be present in the system at a specified pressure and temperature, for a given feed composition. Thus, it was assumed that the residence time inside the reactor is long enough so that all chemical reactions reach equilibrium. The species present in the system were defined according with the reactions considered in the different simulations (Table 2.1, 2.2 and 2.3). Yet, RGIBBS model does not require reaction stoichiometry. The species common to all simulations are H_2, $C_3H_8O_3$, H_2O, CO_2, CO, CH_4, and C.

The yield and the purity on a dry basis of a given species *i* are defined as depicted in equations 3.13 and 3.14, respectively.

$$\mathrm{yield}_i = \frac{m_{\mathrm{i,produced}}}{m_{\mathrm{crude\ (feed)}}} \qquad (3.13)$$

$$\mathrm{purity}_{i,dry\ basis}(\%) = \frac{m_{\mathrm{i,out}}}{\sum_{i=1}^{N} m_{\mathrm{i,out}} - m_{\mathrm{H_2O,out}}} \times 100 \qquad (3.14)$$

$m_{\mathrm{crude\ (feed)}}$ is the molar flow rate of crude glycerol in the feed, $m_{\mathrm{i,produced}}$ is the molar flow rate of species *i* produced and $m_{\mathrm{i,out}}$ is the molar flow rate of species *i* in the output stream of the RGIBBS reactor (thermodynamic equilibrium).

There are some cases where simulations cannot be performed by simply using a single RGIBBS reactor. This is the case when one aims, for example, to simulate the autothermal reforming process with in situ hydrogen separation. In order to simulate a H_2-selective membrane reactor (MR), a sequential modular approach is implemented as represented in Figure 3.1. The membrane reactor is divided into several successive glycerol sub-reformers and membrane sub-separators. The latter is a process unit that separates chemical species according to a specified split fraction or flow, which in practical applications is linked to factors like membrane's selectivity, permeability, thickness, area and process conditions (e.g. temperature and pressure across the membrane). In this particular case, $m_{i,out}$ (of eqs. 3.13 and 3.14) represents the molar flow rate of species *i* in the output stream of the *N*+1 sub-reformer plus the sum of the molar flow rates of species *i* in the permeate stream of the *N* sub-separators. The hydrogen separation factor, $f\mathrm{H}_2$, is described by equation 3.15, where $m_{\mathrm{H}_2,k}$ is the molar flow rate of hydrogen in the permeate stream of sub-separator k and $m_{\mathrm{H}_2,k+1}$ is the molar flow rate in the output of the sub-reformer *N*+1.

$$f\mathrm{H}_2 = \frac{\sum_{k=1}^{N} m_{H_2,k}}{\sum_{k=1}^{N} m_{H_2,k} + m_{\mathrm{H}_2,N+1}} \tag{3.15}$$

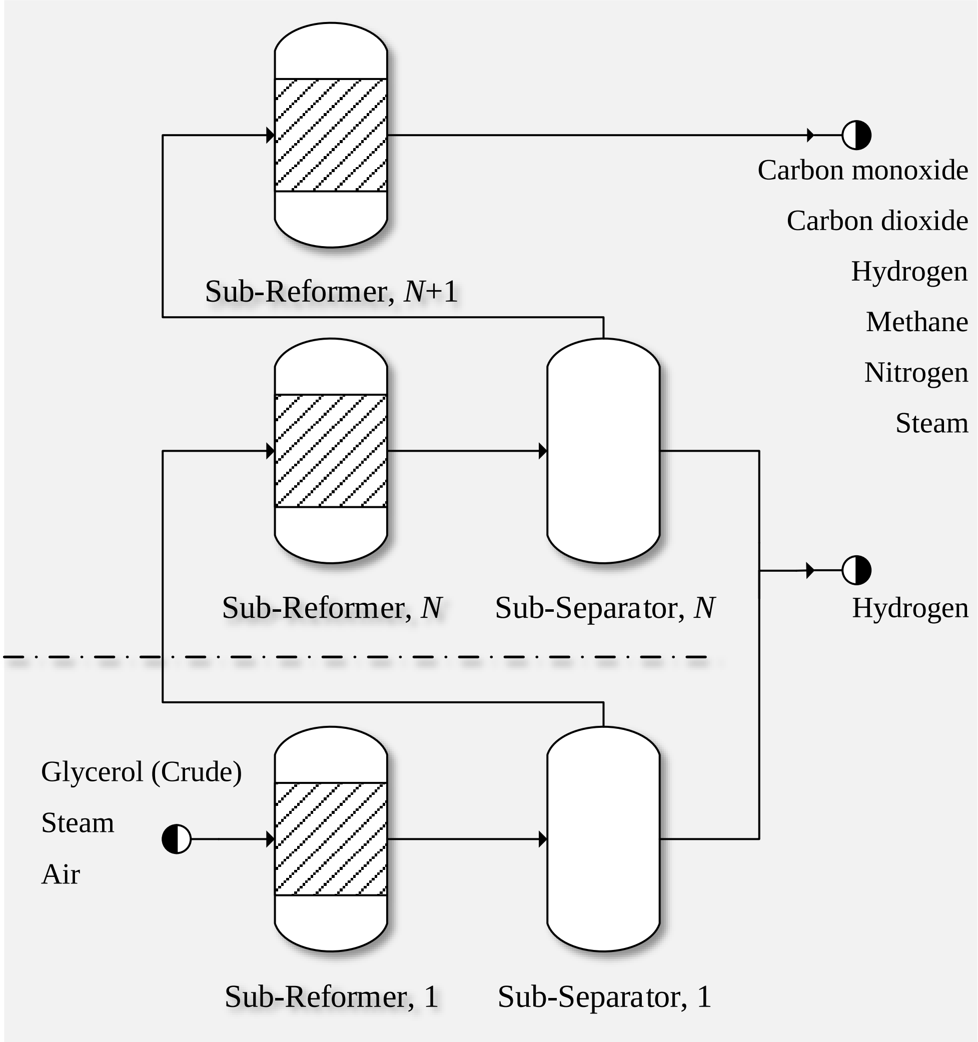

Figure 3.1. Sequential modular approach diagram of the MR.

The number of sub-separators needed in the sequence depends on the global separation factor that one wants to set for the simulation. The higher the separation factor, the higher the number of sub-separators needed. A similar methodology has been implemented in other studies [19, 20, 23]. In order to set the pretended hydrogen separation factor, a *design spec* is created in the simulation. During the design specification, Aspen iterates its calculation sequence through a range of values provided for the independent variable (fraction of hydrogen entering the k sub-separator that is permeated), in order to obtain a specified result for a dependent variable ($f$$H_2$).

To simulate the sorption-enhanced autothermal reforming process of glycerol, i.e. ATR with CO_2 capture, three additional components were defined: calcium oxide (sorbent), calcium carbonate and calcium hydroxide (reaction products – cf. Table 2.2).

There are several parameters that can be adjusted in the simulation model. For the reactor, there are two out of three process conditions that must be specified: temperature, pressure and heat duty. In this work the reactor is always assumed to be isothermal so the temperature and pressure are the chosen parameters to be specified.

Regarding the input stream, it must be specified not only its relative composition but also the pressure and the temperature of its constituents, due to the influence that these properties have on the reactor conditions. The inlet stream conditions were always defined to be the same as inside the reactor, except for the study of the energetically neutral conditions once the inlet temperature has influence on the heat duty of the reactor.

CHAPTER IV – Results and Discussion

4.1. Comparison of main glycerol reforming methods

In order to further understand the major characteristics, advantages and drawbacks of the reforming processes, this work starts with a comparison of steam reforming (SR), autothermal reforming (ATR), dry reforming (DR) and dry autothermal reforming (DATR) methods based on a thermodynamic analysis whose methodology was described in chapter III.

In the different glycerol reforming processes, there is a group of reactions that could be considered depending on the species that are present in the system (nonstoichiometric method). For this case it was considered that $C_3H_8O_3$, H_2, H_2O, CH_4, CO, CO_2, C and O_2 (only for the ATR and DATR processes) are the existing compounds in the system and the possible reactions are depicted in Table 2.1.

4.1.1. Temperature influence on the thermodynamic equilibrium

Firstly it was done a thermodynamic analysis of the main reforming technologies for hydrogen production from glycerol to study the influence of the temperature on the equilibrium compositions behavior. The thermodynamic comparison of the four processes in a traditional reformer was performed for temperatures in the range of 600-1000 K and atmospheric pressure. A water to glycerol feed ratio (WGFR) of 3 was set for the steam and autothermal reforming processes and an oxygen to glycerol feed ratio (OGFR) of 0.6 was set for the latter. Regarding the dry and dry autothermal reforming processes, a carbon dioxide to glycerol feed ratio of 1 was stablished whereas an OCGFR of 0.6 was set for the DATR.

The results of every simulation present complete glycerol conversion throughout the entire temperature range for the four different processes. The same behavior is observed for oxygen conversion in the ATR and DATR processes. Thus, this fact means that the decomposition and oxidation forward reactions are always complete.

Figure 4.1 illustrates the yield of the species considered in the system in the thermodynamic equilibrium for the SR, ATR, DR and DATR processes in a traditional reformer. The curves of H_2O for SR and ATR processes (Figure 4.1 (a) and (b)) and the curves of CO_2 for DR and DATR processes (Figure 4.1 (c) and (d)) represent the ratio of the molar flow rate of these compounds in the outlet stream of the reactor to the molar flow rate of glycerol in the feed.

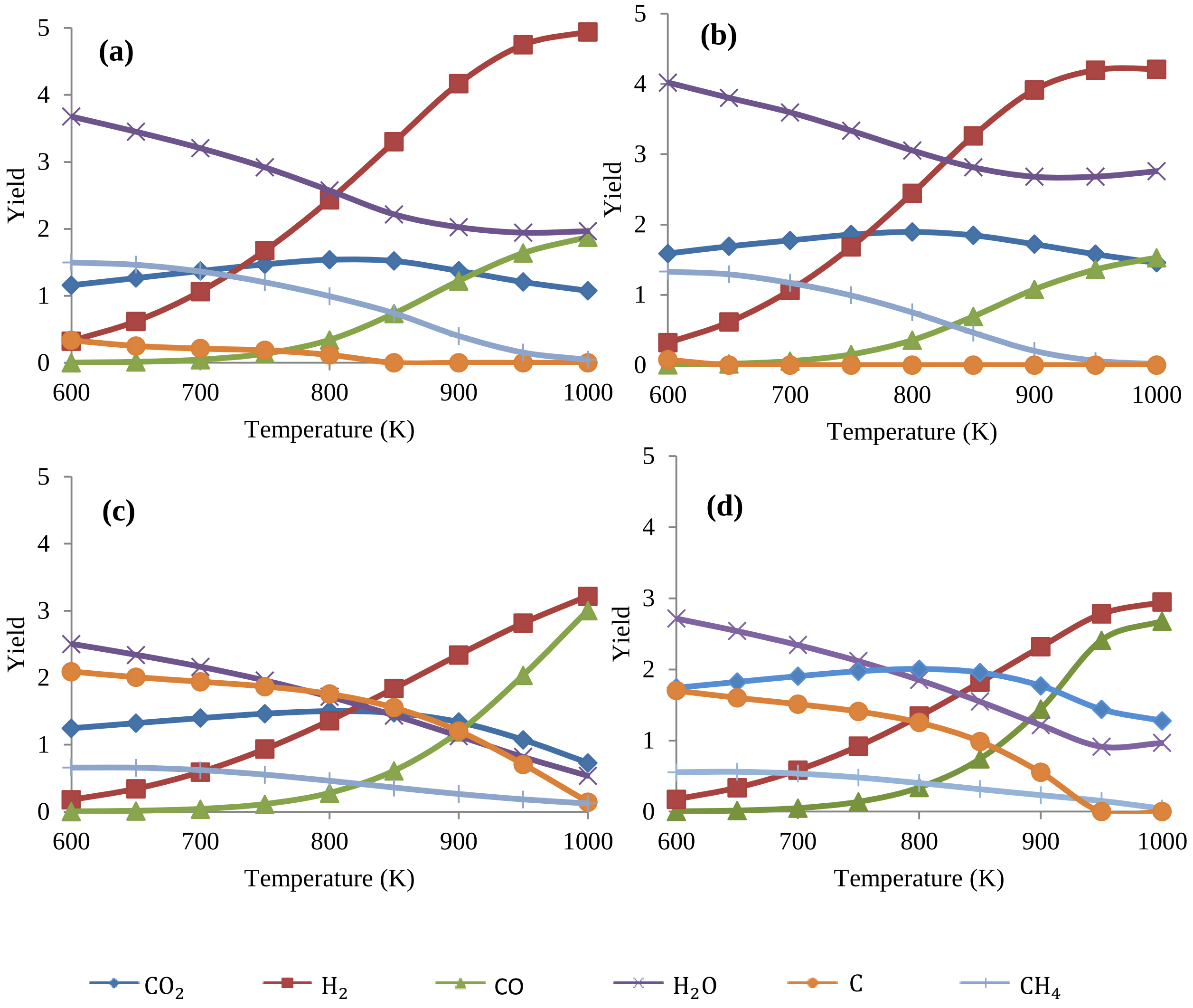

Figure 4.1. Yield in thermodynamic equilibrium as a function of temperature at atmospheric pressure: (a) Steam reforming with WGFR = 3, (b) Autothermal reforming with WGFR = 3 and OGFR = 0.6, (c) Dry reforming with CGFR = 1, (d) Dry autothermal reforming with CGFR = 1 and OGFR = 0.6.

As depicted in Figure 4.1 (a) and (b), the equilibrium yields show a similar trend in both SR and ATR processes, though there are some differences which can be explained by the presence of oxygen in the autothermal reforming process. The yield of H_2 and CO_2 increase with temperature up to a maximum and then suffer a modest decrease, only evident in CO_2 profile. This behavior can be explained by considering both water-gas shift (WGS) and methanation reactions (cf. Table 2.1). At low temperatures, the highly exothermic methanation reaction (equation 2.6) is favoured. This explains the maximum yield not only of methane but also of water, which is above the feed ratio value of 3. As temperature increases, WGS reaction becomes dominant while methanation reaction is inhibited. A stabilization of CO_2 and H_2 is observed at high temperatures due to the enhancement of reverse WGS (RWGS). Plus, the stabilization of H_2 happens at higher temperatures than CO_2 because while the latter is only being consumed by reverse water gas shift reaction, H_2 is also being saved by the inhibition of methanation (3 mol of H_2 per mol of CH_4) reaction. At temperatures >950 K and > 1000 K, for the autothermal and steam reforming processes, respectively, methane is no longer produced and the yield of H_2 drops because RWGS becomes the only dominant reaction.

Between 600 K and 850 K, the behavior of H_2 and CO yields is practically the same for ATR and SR processes. On the other hand, there is less solid carbon in the equilibrium for the autothermal process, which is a result of both carbon and carbon monoxide oxidation reactions (equations 2.20, 2.21 and 2.17, respectively). The latter reaction is favoured over carbon formation from carbon monoxide (equation 2.9). Furthermore, the oxidation reactions of glycerol and methane (represented by equations 2.16 and 2.19, respectively) are responsible for the higher yields of CO_2 and H_2O in the equilibrium of the ATR process at low temperatures. Above 850 K, temperature at which reverse WGS reaction becomes dominant, the yield of hydrogen in the SR process becomes higher than in the ATR. This can be explained by the fact that the reverse WGS reaction (equation 2.5) is more favoured in ATR due to the presence of the CO_2 that is produced by partial oxidation of glycerol (equation 2.13). This also results in more water in the system and consequently the methanation reaction is suppressed at a lower temperature compared to the SR process. Moreover, the carbon monoxide yield in the ATR process is inferior to the one in SR process. This fact is observed because the partial oxidation reaction of glycerol (equation 2.13), which is dominant among oxidation reactions at higher temperatures, produces less number of moles of CO than the decomposition of glycerol reaction (equation 2.4), as per stoichiometry.

Figure 4.1 (c) and (d) depicts the yields in the thermodynamic equilibrium as a function of temperature for the dry and dry autothermal reforming processes, respectively. In contrast with ATR and SR processes, the yield of CO suffers a sharper increase with temperature whereas the yield of H_2 shows a softer increase, which leads to lower hydrogen to carbon monoxide ratios. At low temperatures, CO is not present in the thermodynamic equilibrium because it is completely converted into CH_4, H_2O and C trough methanation (equation 2.6) and carbon formation (equations 2.9 and 2.11) reactions. The presence of CO_2 as well as the absence of H_2O in the feed also promotes carbon formation via reactions 2.11 and 2.12, which explains the much larger amount of solid carbon in these processes. Furthermore, reactions 2.11 and 2.12 compete thermodynamically with methanation reaction (equation 2.6) due to the fact that hydrogen is a reagent in these reactions. Consequently, the methane yield at low temperatures in these processes is lower than in SR and ATR. Besides that, more water is produced due to the stoichiometry of carbon formation reactions (the water yield represented in figure 4.1 (c) and (d) is lower, though, because no steam is fed as it is in the SR and ATR processes). At higher temperatures, the reverse of WGS reaction, which is favoured by high temperatures and excess of CO_2, becomes dominant. This reaction is then responsible for the greater amount of carbon monoxide in the equilibrium as well as for the lower production of hydrogen. Moreover, the yields of water, methane and coke decrease with temperature as a result of the inhibition of methanation reaction (equation 2.6) and coke formation reactions (equations 2.11 and 2.12), which are exothermic and consequently less favoured at high temperatures. Regarding coke formation, its complete inhibition happens at considerably higher temperatures compared with SR and ATR processes' behaviors. Solid carbon formation can be completely inhibited at 1000 K and 950 K for the DR and DATR, respectively.

The yields of CO_2 and H_2O in the thermodynamic equilibrium for the DATR process are higher than for the DR. The partial oxidation reactions of glycerol are responsible for the higher values of carbon dioxide yield whereas the latter is responsible for the limitation of the WGS reaction and consequently for the increase in steam. Furthermore, there is less carbon in DATR process and its complete inhibition takes place at a lower temperature due to the presence of a higher amount of steam, which limits the carbon formation reactions depicted by equations 2.11 and 2.12.

In the next section, the results of thermodynamic evaluation focus on hydrogen and syngas production. For further analysis of the behavior of the other species present in the system, as a function of the analyzed parameters/operating conditions, please see Appendix B. Table 4.1 presents the conditions under each one of the technologies were evaluated with respect to hydrogen and syngas production.

Table 4.1. Conditions evaluated in the different glycerol reforming processes.

Reforming technology	Temperature range (K)	Pressure range (atm)	Feed composition range
SR	600-1000	1-20	1/3-12 $C_3H_8O_3/H_2O$ molar ratio
ATR	600-1000	1-20	1/3-12/0-3 $C_3H_8O_3/H_2O/O_2$ molar ratio
DR	600-1000	1-20	1/0.5-3 $C_3H_8O_3/CO_2$ molar ratio
DATR	600-1000	1-20	1/0.5-3/0-3 $C_3H_8O_3/CO_2/O_2$ molar ratio

4.1.2 Hydrogen and syngas production – Steam reforming

Figures 4.2 (a) and (b) show the H_2 and CO equilibrium yield as a function of temperature and pressure, respectively. As previously observed in Figure 4.1, hydrogen and carbon monoxide yields increase with temperature whereas H_2/CO ratio tends to decline. The latter behavior is a result of RWGS which becomes dominant with temperature. In contrast, pressure has an unfavorable effect on both H_2 and syngas (total of H_2 and CO) yield and little effect on the H_2/CO ratio (please take the yy axis scale into account). This effect is observed because the increase in the system's pressure leads to a shift in the equilibrium to the side of the lesser number of moles in order to counteract the pressure rise. Although glycerol decomposition reaction has less number of moles in the reactants side, the simulation results show complete conversion of glycerol throughout the entire pressure range. So, the decrease on H_2 and CO yields is a result of methanation reaction (2.6), which is favoured at higher pressures. The slight increase in ratio can be a result of the inhibition of RWGS (dominant reaction at 1000 K) caused by methanation reaction, which consumes one and three moles of carbon monoxide and hydrogen, respectively, and produces not only methane, but also water.

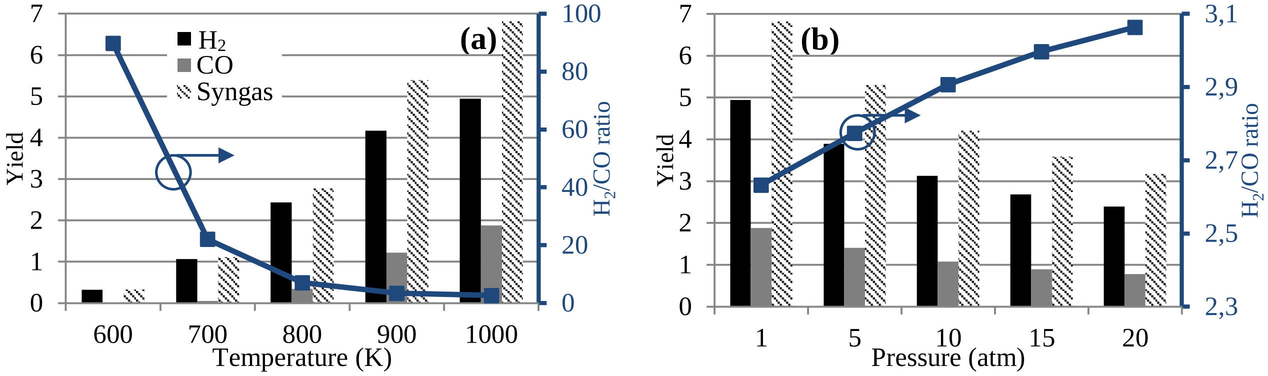

Figure 4.2. Yield of H_2, CO and syngas and H_2/CO ratio in the thermodynamic equilibrium for steam reforming as a function of: (a) temperature at atmospheric pressure and WGFR = 3; (b) pressure at 1000 K and WGFR = 3.

The effect of water/glycerol molar ratio on H_2, CO and syngas (total of H_2 and CO) production is depicted in Figure 4.3. The increase of steam in the feed results in the rise of hydrogen production as well as in the inhibition of CO formation; consequently the H_2/CO ratio increases. This happens due to the fact that WGS reaction (equation 2.5) is favoured by the excess of steam. On the other hand, the WGFR almost does not influence yield of syngas in the equilibrium.

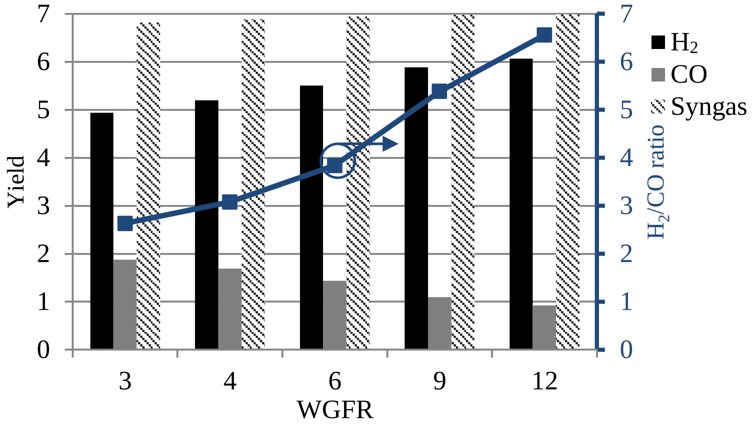

Figure 4.3. Yield of H_2, CO and syngas and H_2/CO ratio in the thermodynamic equilibrium for steam reforming as a function of WGFR at atmospheric pressure and T = 1000 K.

4.1.3 Hydrogen and syngas production – Autothermal reforming

The Figures 4.4 (a) and (b) depict the H_2, CO and syngas equilibrium yields for ATR as a function of temperature and pressure, respectively. As discussed in section 4.1.1, the compositions behavior is the same for SR and ATR processes up to a certain temperature. Afterwards, the increase in H_2 is less pronounced (or even decreases) due to the less exothermic partial combustion reaction (equation 2.13) that occurs in the presence of oxygen. This reaction gives one and two moles of CO_2 and CO, respectively, whereas glycerol decomposition gives three moles of CO. Consequently, the RWGS at high temperatures is less pronounced for SR process. The pressure effect on the ATR process with respect to H_2 and syngas production is similar to the effect that was observed on the SR process in the pressure range studied.

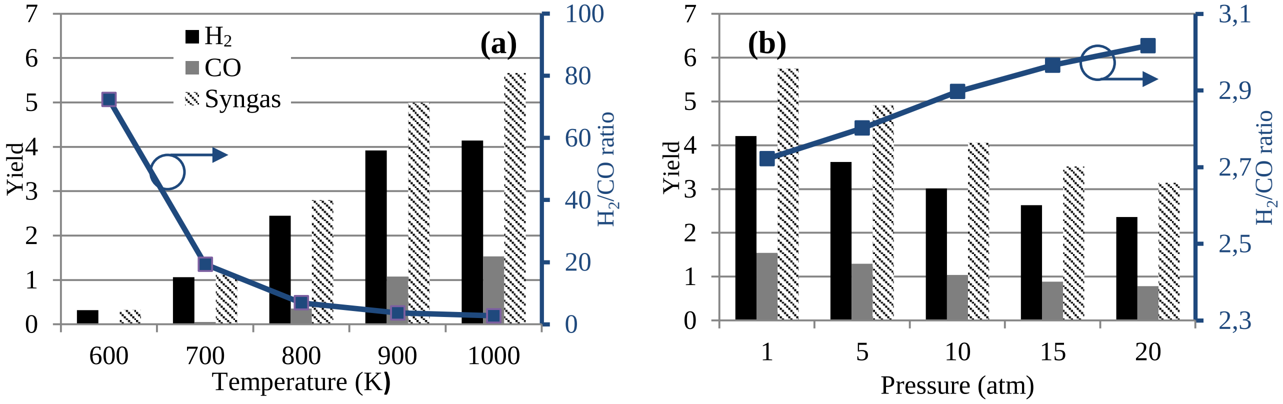

Figure 4.4. Yield of H_2, CO and syngas and H_2/CO ratio in the thermodynamic equilibrium for autothermal reforming as a function of: (a) temperature at atmospheric pressure, WGFR = 3 and OGFR = 0.6; (b) pressure at T = 1000 K, WGFR = 3 and OGFR = 0.6.

The effect of WGFR over the autothermal reforming of glycerol is presented in Figure 4.5 (a). As observed in the SR process, the H_2 production grows as long as CO production diminishes with increasing WGFR ratios. As shown in Figure 4.5 (b), the presence of oxygen in the feed has a negative effect on both hydrogen and syngas production due to the enhancement of partial oxidation reactions, whose effect is previously explained in this section.

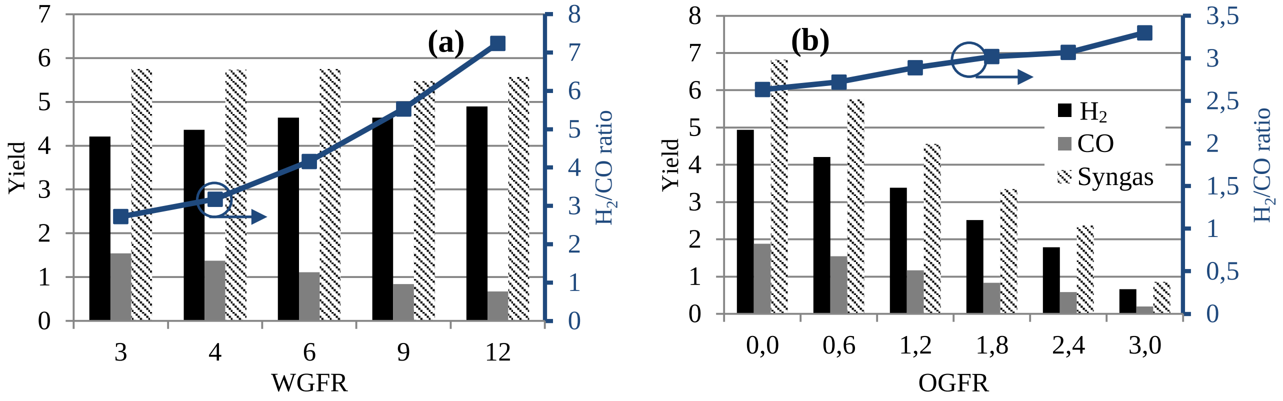

Figure 4.5. Yield of H_2, CO and syngas and H_2/CO ratio in the thermodynamic equilibrium for autothermal reforming as a function of: (a) WGFR at atmospheric pressure, T = 1000 K and OGFR = 0.6; (b) OGFR at atmospheric pressure, T = 1000 K and WGFR = 3.

4.1.4 Hydrogen and syngas production – Dry reforming

Figure 4.6 (a) presents the results of the thermodynamic analysis with respect to the temperature effect on H_2, CO and syngas equilibrium yields for the DR. In this process, the increase in the yield of CO with temperature is greater than in ATR and SR processes, as described before (section 4.1.1), which results in lower H_2/CO ratios. This behavior is a consequence of the high amounts of carbon dioxide in the feed stream. At 1000 K the H_2/CO relation is close to one.

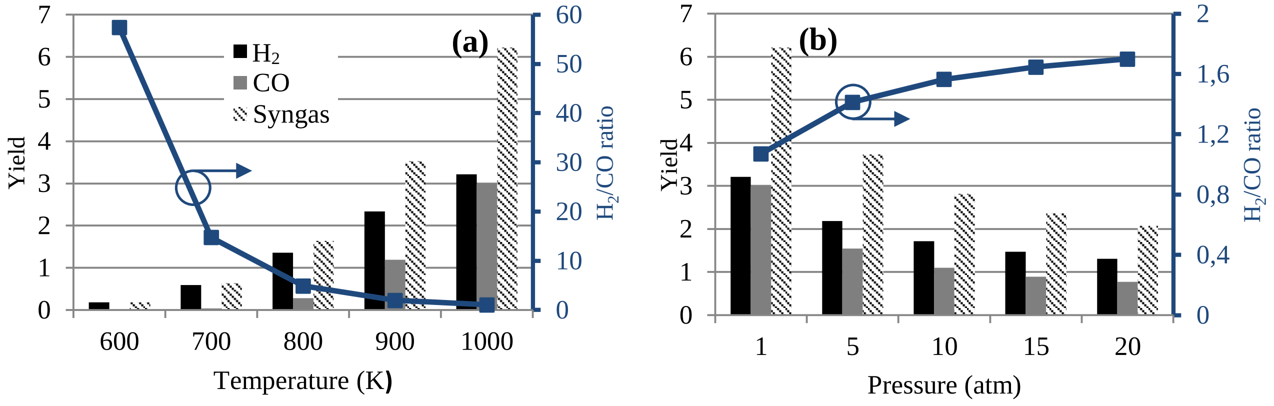

Figure 4.6. Yield of H_2, CO and syngas and H_2/CO ratio in the thermodynamic equilibrium for dry reforming as a function of: (a) temperature at atmospheric pressure and CGFR = 1; (b) pressure at 1000 K and CGFR = 1.

Analyzing Figure 4.6 (b) it is possible to verify that the yield of CO and H_2 decrease with pressure whereas the H_2/CO ratio suffers a slight increase. The decline of CO yield is more pronounced than the one of H_2 because CO is being consumed not only by the methanation reaction (equation 2.6) but also by the WGS reaction (equation 2.5) as a result of the water formed in the previous reaction; moreover, the WGS also leads to hydrogen production.

The effect of carbon dioxide to glycerol ratio (CGFR) in the feed is depicted in Figure 4.7. The elevation of the CGFR results in a significant increase in the CO production. This occurs because CO_2 favors the reverse of WGS reaction.

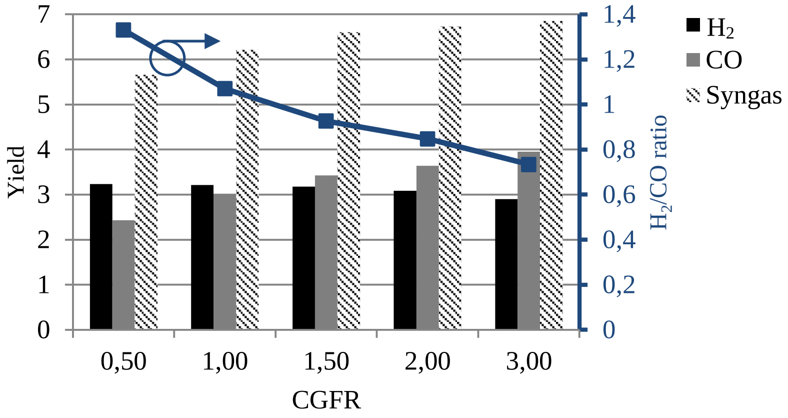

Figure 4.7. Yield of H_2, CO and syngas and H_2/CO ratio in the thermodynamic equilibrium for dry reforming as a function of CGFR at atmospheric pressure and T = 1000 K.

4.1.4 Hydrogen and syngas production – Dry autothermal reforming

Figure 4.8 (a) shows the effect of temperature on hydrogen and carbon monoxide yields as well as on syngas ratio for the DATR. The results for this process follow the same trend as for DR. However, the yield values are lower in this process, which is a result of the partial oxidation (PO) reactions that take place in the reaction medium. The PO reaction produces not only H_2 and CO but also CO_2, which is responsible for limiting the WGS reaction and consequently decreasing the H_2 yield and the H_2/CO ratio.

The pressure increase only favors methanation reaction and consequently has a negative effect on both H_2 and CO yield, as represented in Figure 4.8 (b). Nevertheless, the H_2/CO ratio is almost constant in the pressure range studied; it is only slightly favoured, for the reasons described in the previous process – WGS reaction promotion as a consequence of the water formed via methanation reaction.

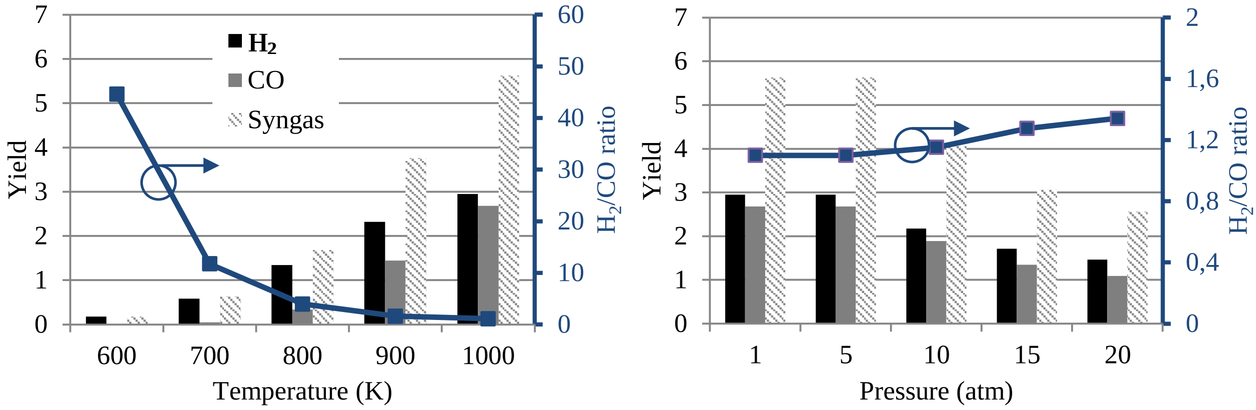

Figure 4.8. Yield of H_2, CO and syngas and H_2/CO ratio in the thermodynamic equilibrium for dry autothermal reforming as a function of: (a) temperature at atmospheric pressure and CGFR = 1 and OGFR = 0.6; (b) pressure at 1000 K, CGFR = 1 and OGFR = 0.6.

The effect of CGFR on H_2 and CO yield is depicted in Figure 4.9 (a). As observed for DR, the yield of H_2 decreases with CGFR whereas the yield of CO rises. In the DATR reforming, the partial oxidation reactions produce two moles of carbon monoxide per mole of glycerol, which is less than the moles produced by decomposition of glycerol. This fact explains the slighter increase on syngas with CGFR compared with DR process.

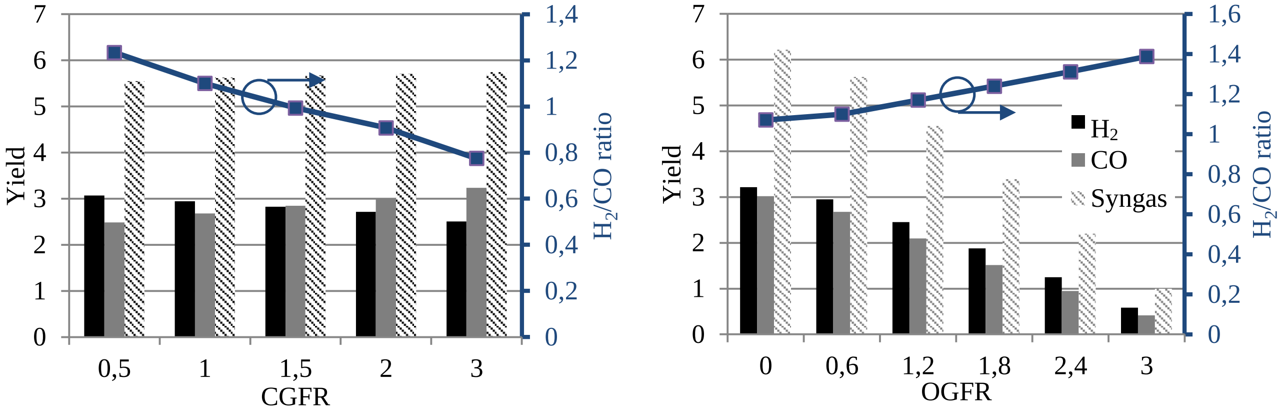

Figure 4.9. Yield of H_2, CO and syngas and H_2/CO ratio in the thermodynamic equilibrium for dry autothermal reforming as a function of: (a) CGFR at atmospheric pressure, T = 1000 K and OGFR = 0.6; (b) OGFR at atmospheric pressure, T = 1000 K and CGFR = 1.

Figure 4.9 (b) shows the effect of OGFR on the equilibrium yields of hydrogen, carbon monoxide and syngas. Both H_2 and CO yields decrease with OGFR because PO reactions produce less CO and more CO_2 than the decomposition of glycerol. Consequently the RWGS becomes more favoured, which explains the H_2 yield drop with OGFR. The H_2 does not suffer a decrease as sharper as CO, which results in an increase on the H_2/CO ratio.

The ATR is a process for producing hydrogen that is attractive from the energetic point of view. As observed in the previous sections 4.1.1 and 4.1.3, the yields' behavior is similar in both ATR and SR processes. At high temperatures, at which methane formation is completely inhibited, the hydrogen yield for ATR is lower though. However, there are some solutions (eg. in situ separation of CO_2 and H_2) that may maximize the hydrogen yield to the stoichiometric value of 7 while operating without an external heating input. These solutions have not been investigated by other authors yet. Thus, section 4.2 is exclusively dedicated to the study of this process.

4.2. Autothermal reforming

In this section a detailed study of the autothermal reforming process is reported. In addition to temperature, pressure, WGFR and OGFR, there are other factors that may influence the process performance and their effects are described in the following subsections.

4.2.1 Effect of N_2 in the feed composition

In the ATR process, oxygen is added into the system in order to promote oxidation reactions and consequently generate the required heat for the reforming reaction. As an alternative for pure oxygen, air can be fed into the system so the purification step of oxygen can be suppressed from the process. However, the presence of other gases can influence the compositions in the thermodynamic equilibrium. The effect of nitrogen, which is the major compound of air (~79 vol. %), is depicted in Figure 4.10.

From Figure 4.10, one can observe that nitrogen has a slightly positive effect on both hydrogen and CO equilibrium yields for the autothermal reforming process. This phenomenon can be explained by the dilution effect. The presence of an inert gas in the equilibrium system at constant pressure reduces the partial pressures of the reactive gases. According to the *Le Chatelier*'s principle, a decrease in the partial pressure leads to a shift in the reaction equilibrium toward the direction with the greater number of moles of gas. As observed in section 4.1.1, glycerol is completely converted for every conditions studied. Thus, the dilution effect does not influence reaction 2.4 neither the WGS but inhibits the methanation reaction and consequently the yield of H_2 and CO increases (even if very slightly only).

The effect of nitrogen is not very pronounced due to the low ratio of nitrogen to oxygen in the atmosphere, which is about 4:1. Hence, one can anticipate that it might be advantageous to directly add air into the system once it will reduce the costs associated with the purification of oxygen; even so, a detailed analysis should be done because larger reactors are required and nitrogen needs to be separated afterwards. These aspects are however out of the goal of this work.

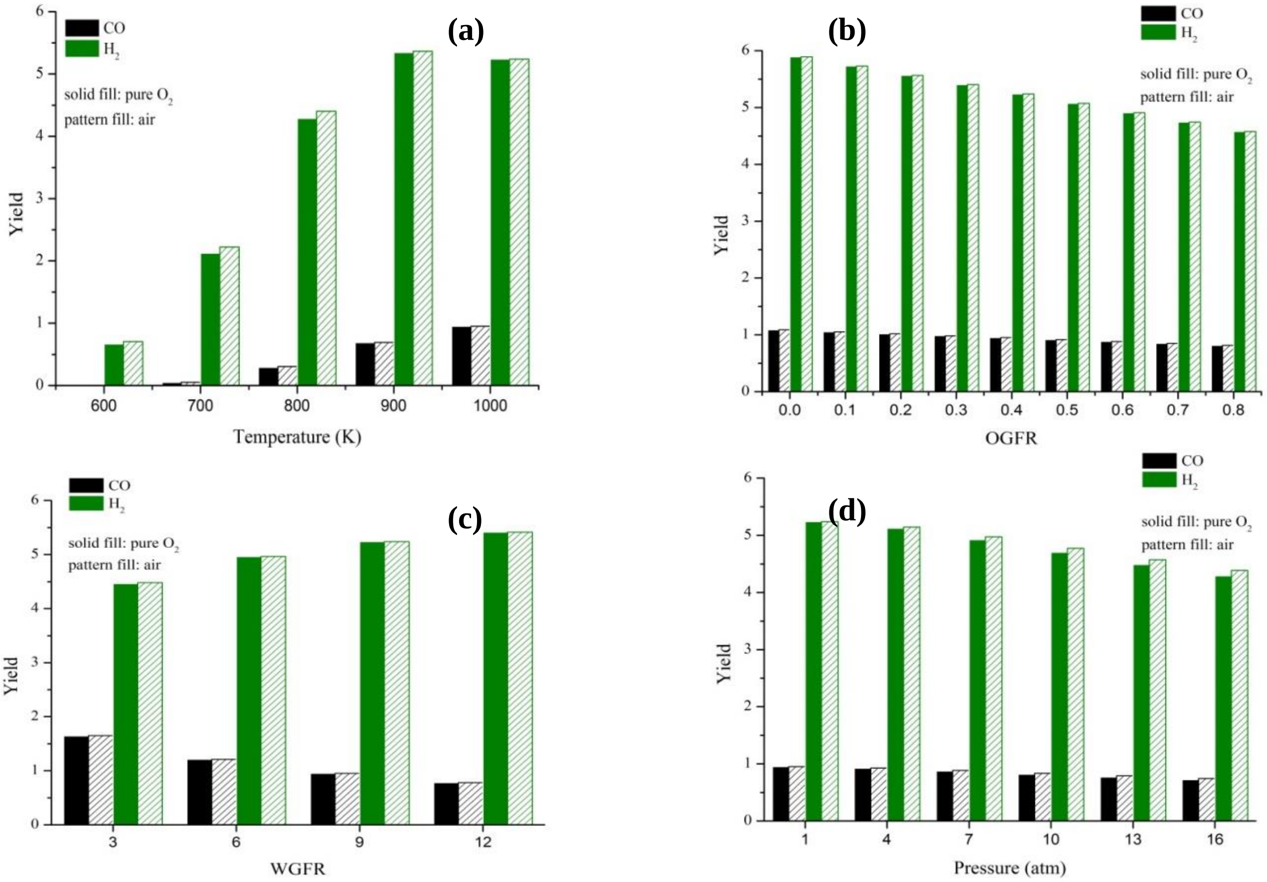

Figure 4.10. Comparison of the yields of CO and H_2 in the thermodynamic equilibrium in the presence and absence of nitrogen in the feed as a function of: (a) temperature at atmospheric pressure, WGFR = 9 and OGFR = 0.4; (b) OGFR at atmospheric pressure, T = 1000 K and WGFR = 9; (c) WGFR at atmosferic pressure, T = 1000 K and OGFR = 0.4; (d) pressure at T = 1000 K, WGFR = 9 and OGFR = 0.4.

4.2.2 Effect of glycerol crude composition

Generally, crude glycerol obtained from biodiesel production contains some impurities such as methanol, soap, catalyst and organic matter. The composition of the crude depends on the type of feedstock and process technologies applied. The quality of crude glycerol is influenced, for example, by catalyst type and quantity, recovery methods and unreacted methanol. Hansen et al.

[25] determined the chemical composition of eleven samples of crude glycerol collected from seven different biodiesel manufacturers. A resume of their results is represented in Table 4.2.

Table 4.2. Characteristics of crude glycerol from different biodiesel plants.

Content	Range	Average
Glycerol (wt. %)	38.4 – 96.5	72.4
Moisture (wt. %)	0.0 – 16.1	5.5
Ash (wt. %)	0.0 – 29.4	5.2
Methanol (wt. %)	<0.01 – 13.94	4.12
MONG (wt. %)[B]	1.0 – 57.0	13.9

[B] MONG: matter organic non-glycerol. Defined as 100-[glycerol content (wt. %) + water content (wt. %) + ash content (wt. %)].

The purification process of crude glycerol requires high operating costs [3]. Thus, the aim we envisage is to use crude glycerol as raw material for the autothermal reforming process. In order to simplify the simulations it was assumed that the only compounds present in the crude are glycerol and unconverted methanol (water is also included in the feed composition). In this case, in addition to the reactions depicted in Table 2.1, there are three more that must be taken into account, which are represented in Table 2.3.

Table 4.3 presents the conditions under which crude glycerol autothermal reforming was evaluated. The maximum value for methanol to glycerol mass ratio found in the study of Hansen et al. [25] was approximately 0.22, which corresponds to a molar ratio of 0.63. Yet, the simulations were performed for molar ratios between 0 and 1.5 (0 to 60 mol. % of methanol in crude) in order to take a wider view of the effects of methanol on equilibrium yields of H_2 and CO.

Table 4.3. Conditions evaluated in the autothermal reforming of crude glycerol process.

Crude composition range	Temperature range (K)	Feed composition range
1/0-1.5 $C_3H_8O_3/CH_3OH$	600-1000	1/3-12/0.1-0.8 $(C_3H_8O_3+CH_3OH)/H_2O/O_2$

Figure 4.11 shows the yield and the purity (dry basis) of hydrogen and carbon monoxide as a function of temperature, water to crude glycerol ratio (WCGFR) and oxygen to crude glycerol ratio (OCGFR) at different crude glycerol compositions. The results indicate that the yields of hydrogen

and carbon monoxide obtained from crude glycerol are lower comparing to the case of using pure glycerol for any temperature, WCGFR or OCGFR in study. This results from the decomposition of methanol reaction. Per stoichiometry, reaction (2.25) produces a lesser number of moles of hydrogen and CO than the one from glycerol. Therefore, the amount of H_2 and CO decreases when methanol content in crude glycerol increases. At low temperatures (Figure 4.11 (a)) this effect is attenuated because methanation reaction is dominant under these conditions and consequently the hydrogen that is produced by decomposition and oxidation of glycerol and/or methanol is converted to methane and water. The higher number of moles of hydrogen produced by decomposition and oxidation of pure glycerol is responsible for the greater extent of methanation reaction in this case. Consequently, the yields of hydrogen and carbon monoxide are very similar at low temperatures. However, WGS is also slightly promoted by steam, which explains the existence of hydrogen at low temperatures. This is in accordance with the fact that, for pure glycerol a higher yield of both methane and CO_2 was observed at low temperature (data not shown).

As OCGFR increases, both H_2 and CO yield decreases (Figures 11 (e) and (f), respectively). This is because the partial oxidation of glycerol (equation 2.13) becomes dominant and consequently the decomposition of glycerol is inhibited. Thus, instead of three moles of carbon monoxide produced per mole of glycerol, there is one mole of carbon dioxide and two moles of carbon monoxide. This results in a greater extent of the RWGS reaction, which consumes more H_2.

On the contrary, the purity (dry basis) of H_2 slightly increases with the increase of methanol content in crude glycerol whereas CO purity decreases. This can be explained by the lesser amount of carbon monoxide in the system. As per stoichiometry, the carbon monoxide to hydrogen molar ratio for the decomposition of methanol and glycerol is 1/2 and 3/4, respectively (cf. reactions 2.25 and 2.4).

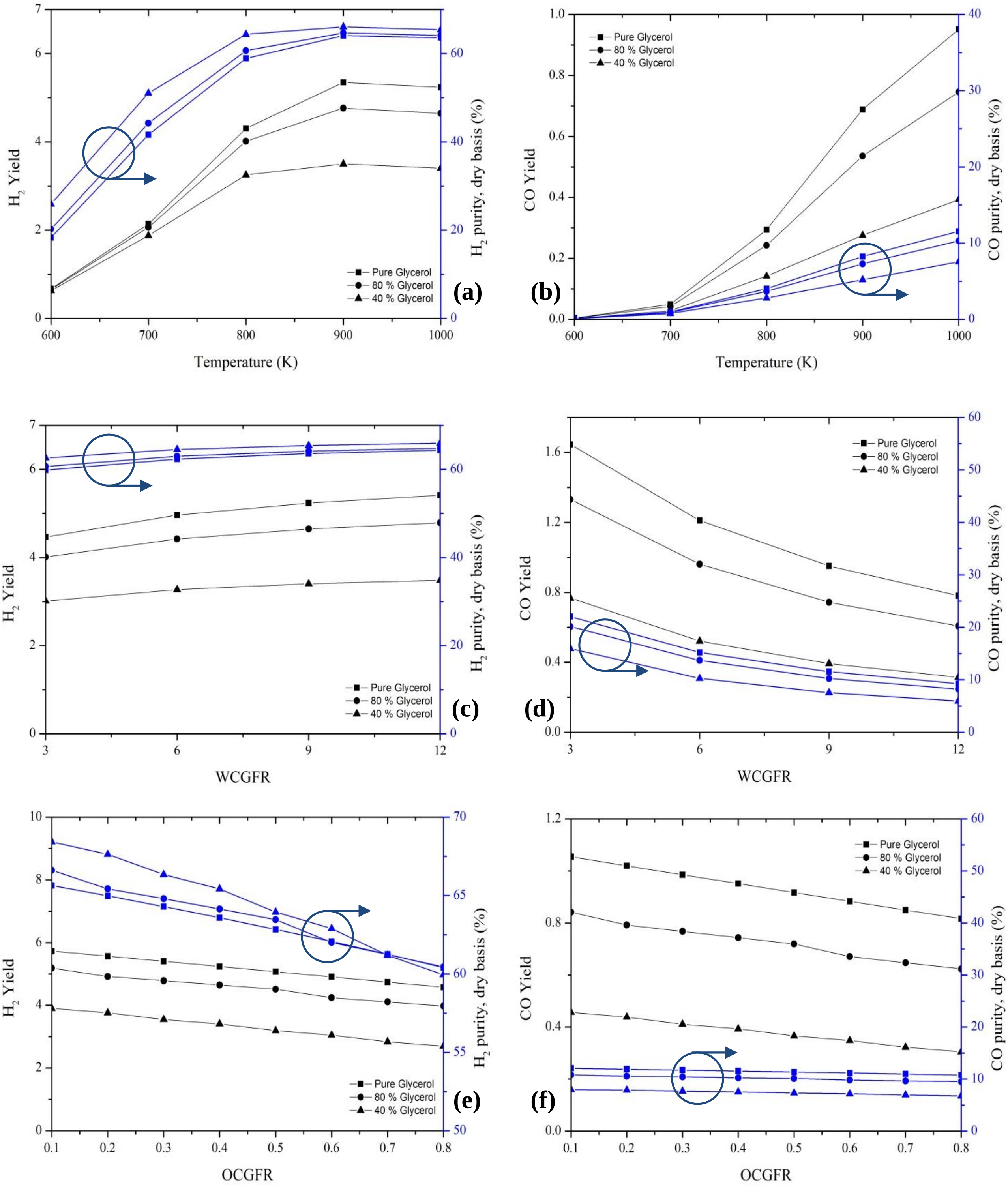

Figure 4.11. Yield and purity of H_2 and CO in the thermodynamic equilibrium as a function of: (a),(b) temperature at atmospheric pressure, WGFR = 9 and OCGFR = 0.4; (c),(d) WCGFR at atmospheric pressure, T = 1000 K and OCGFR = 0.4; (e),(f) OCGFR at atmospheric pressure, T = 1000 K and WCGFR = 9.

4.2.3 Autothermal reforming with H_2 separation – Effect of temperature and glycerol crude composition

A comparison of ATR’s equilibrium compositions with and without hydrogen separation as a function of temperature is represented in Figure 4.12. In the case that there is *in situ* separation of hydrogen (e.g. with a perm-selective membrane), and whatever the temperature, we can observe an increase of both H_2 and CO_2 yield and a decrease of both CO and CH_4 yield. This behaviour can be explained by the enhancement of the WGS reaction, which consumes CO and produces H_2 and CO_2, as well as the inhibition of the methanation reaction. Furthermore, complete inhibition of methanation reaction as well as the maximum yield of hydrogen is reached at lower temperatures.

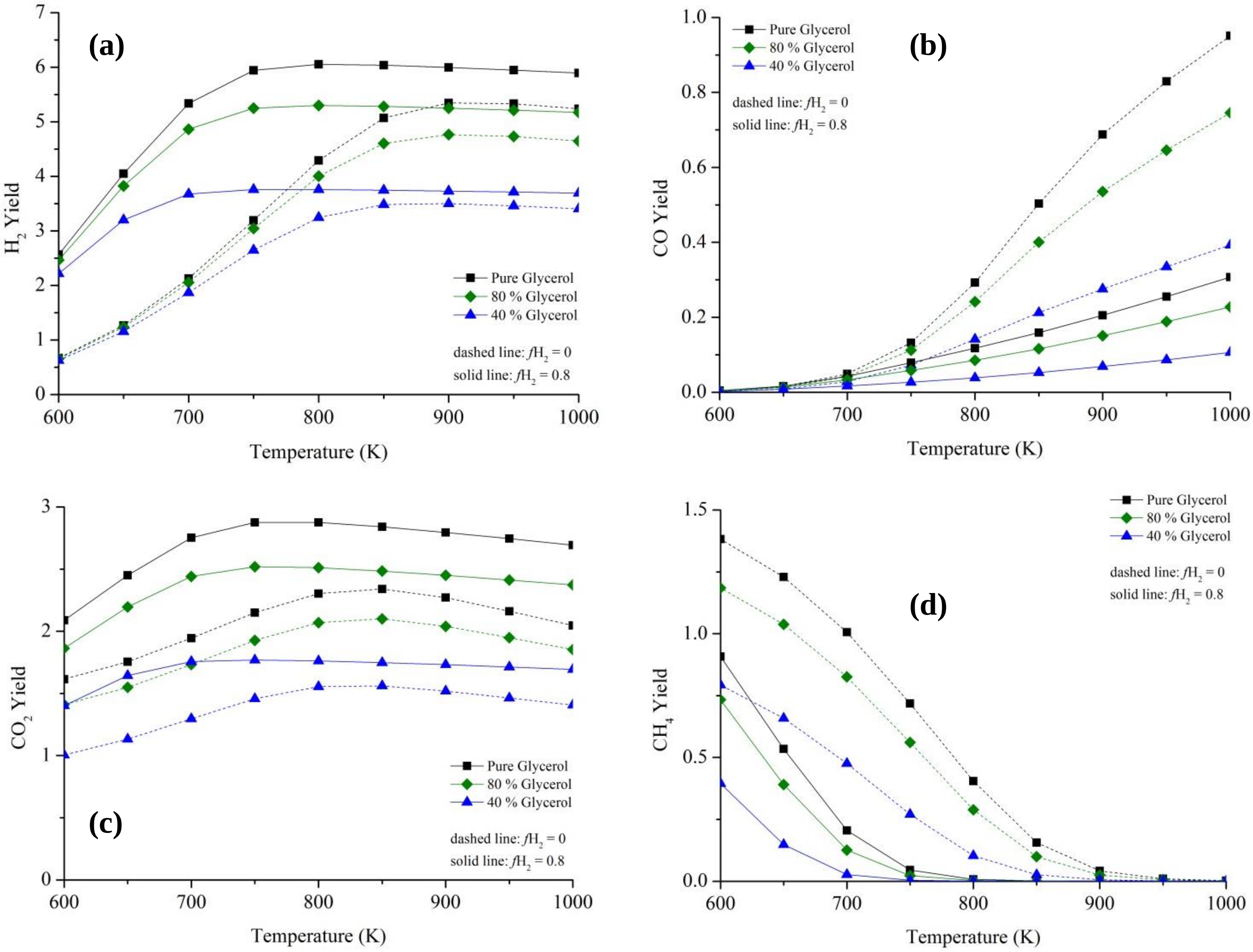

Figure 4.12. Autothermal reforming process with (fH_2=0.8) and without (fH_2=0) H_2 separation, at WCGFR=9, OGCFR = 0.4 and 1 atm; effect of temperature and glycerol crude composition on the yield of (a) hydrogen, (b) carbon monoxide, (c) carbon dioxide and (d) methane.

The yields of the species analysed always rise with increasing content of glycerol in the crude for the reasons above mentioned (section 4.2.2). On the other hand, the hydrogen yield reaches a maximum at lower temperatures when there is less glycerol in the crude. The point of maximum yield of hydrogen corresponds to the almost complete inhibition of methane production. From Figure 4.13, one can also conclude that the H_2/CO ratio is significantly higher when hydrogen is separated from the system, especially at lower temperatures. The WGS reaction, which is favoured under these conditions, is responsible for this behaviour. The H_2/CO ratio also grows with the methanol content in the crude due to the stoichiometry of steam reforming reactions (2.4) and (2.25), i.e. the glycerol steam reforming reaction produces more carbon monoxide (per hydrogen produced) than the methanol one.

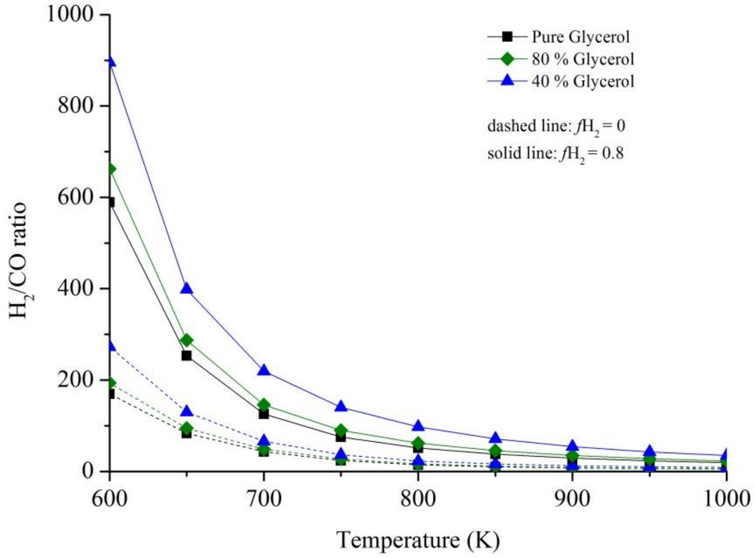

Figure 4.13. Autothermal reforming process with and without H_2 separation, at WCGFR = 9, OCGFR = 0.4 and 1 atm; effect of temperature and glycerol crude composition on H_2/CO ratio.

The removal fraction of hydrogen can vary widely, depending on the type of membrane used in the reactor [27]. So, it is important to study the effect that different removal fractions have on the yields of the existing species in the system. Figure 4.14 represents the yield of hydrogen, carbon monoxide, carbon dioxide and methane as a function of temperature and removal fraction of H_2 for the autothermal reforming of pure glycerol. From Figure 4.14 (a) one can observe that the higher is the removal fraction of hydrogen, the lower is the temperature at which hydrogen yield reaches its maximum value. The reason why this behaviour is observed is that WGS reaction is favoured not only by lower temperature but also by the lack of H_2 in the reaction medium. A similar behaviour is observed for the carbon dioxide yield. For the above-mentioned reasons (section 4.1.1.), in the latter case the maximum yield is attained at even lower temperatures for a fixed removal fraction of hydrogen. On the other hand, the production of CO and CH_4 declines as the removal fraction increases at all temperatures (Figure 4.14 (b) and (d)). The decline is prominent for higher temperatures in the case of CO yield whereas CH_4 yield decreases more sharply for lower temperatures. That suggests that at higher temperature the hydrogen removal (e.g. by a Pd-based membrane) shifts the equilibrium of WGS reaction towards consuming more CO and producing more H_2 and CO_2, while at lower temperature it is mostly acting by inhibiting the methane formation.

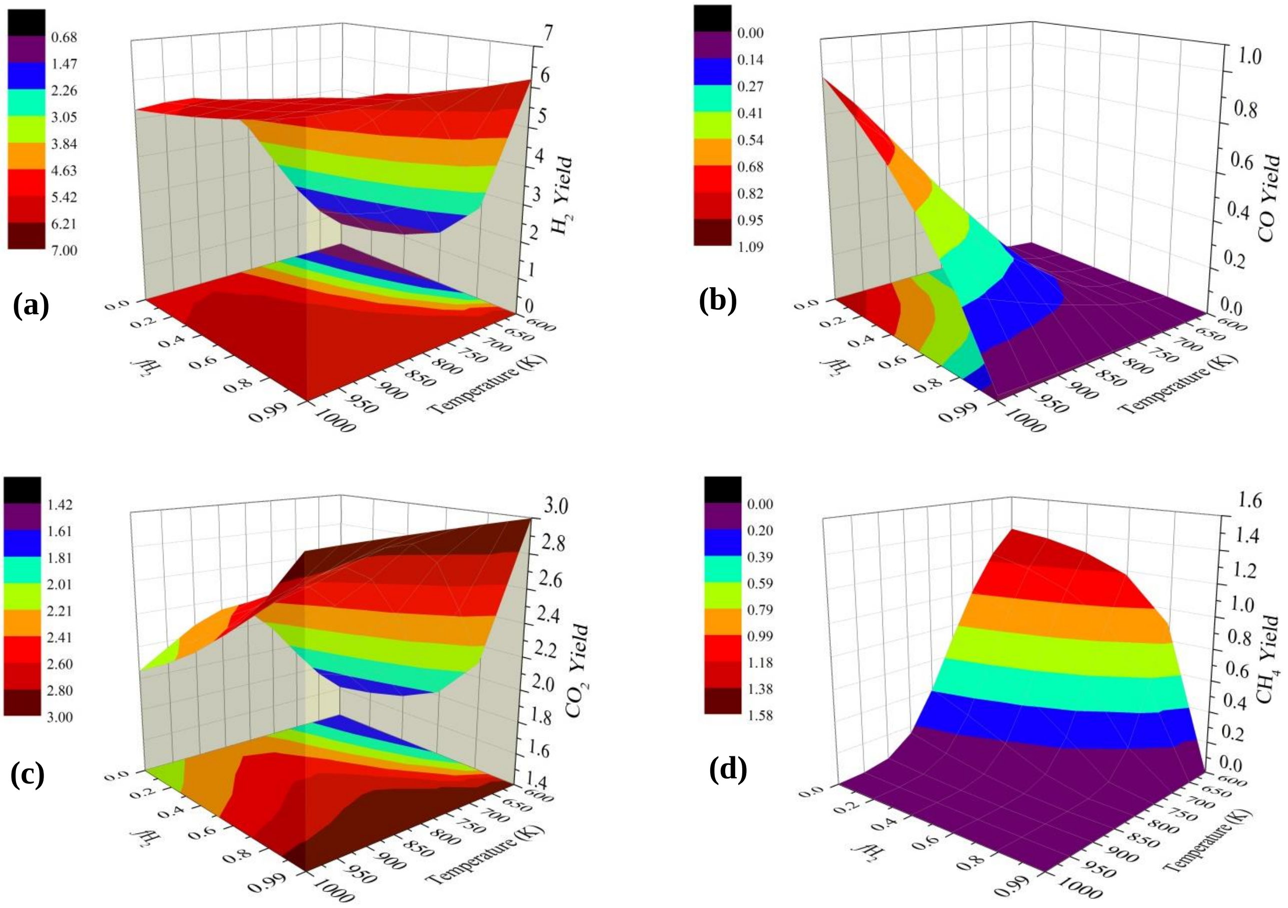

Figure 4.14. Autothermal reforming of pure glycerol, at WGFR = 9, OGFR = 0.4 and 1 atm; effect of temperature and removal fraction of H_2 on the yield of (a) hydrogen, (b) carbon monoxide, (c) carbon dioxide and (d) methane.

4.2.4 Autothermal reforming with CO2 sorption – Effect of temperature and glycerol crude composition

In order to study the autothermal reforming process with CO_2 sorption, it is necessary to consider three additional species in the system: calcium oxide (CaO) sorbent, as well as calcium hydroxide ($Ca(OH)_2$) and calcium carbonate ($CaCO_3$) that are formed through chemical reactions. The reactions where these species are involved are represented in Table 2.2.

Figure 4.15 depicts the yields in the thermodynamic equilibrium of hydrogen, carbon monoxide, carbon dioxide and methane as a function of temperature, for three different crudes, for the autothermal reforming process with and without CO_2 sorption. As expected, CO_2 is totally adsorbed in the form of $CaCO_3$ and $Ca(OH)_2$ according to reactions 2.22 and 2.23 and does not exist in the outgoing stream up to 800 K. From this temperature on, the carbonation of calcium oxide is limited by temperature due to its exothermicity and consequently de yield of carbon dioxide grows (Figure 4.15 (c)). Also, carbon monoxide is not present in the thermodynamic equilibrium mixture up to the same temperature due to the fact that the WGS reaction is favoured by the absence of CO_2 in the reaction medium; therefore, hydrogen yield is improved.

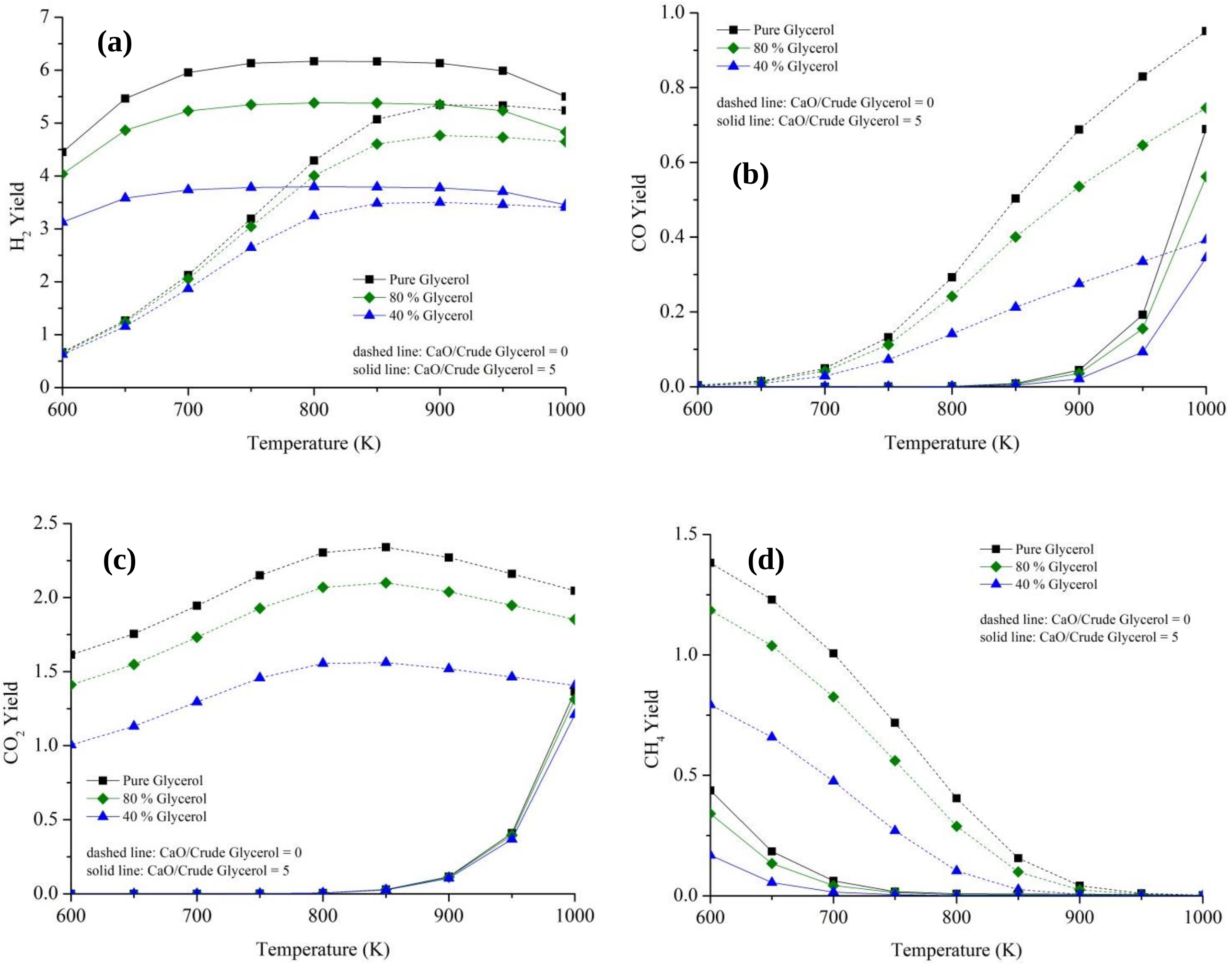

Figure 4.15. Autothermal refoming process with and without CO_2 sorption, at WGFR=9, OGCFR=0.4 and 1 atm; effect of temperature and glycerol crude composition on the yield of (a) hydrogen, (b) carbon monoxide, (c) carbon dioxide and (d) methane.

Figure 4.16 represents the H_2/CO ratio as a function of temperature for the autothermal reforming process with and without CO_2 sorption. When there is CO_2 sorption, the ratio is considerably higher, which is a result of the enhancement of the WGS reaction, particularly at lower temperatures. The difference between the behaviour observed for H_2 separation and CO_2 sorption is that in the latter the removal fraction attained is one up to 800 K whereas for the hydrogen removal simulation a fraction of 0.8 was set for the entire temperature range. Thus, the ratio in this case is enormously superior to the one when there is only H_2 separation from the reaction medium.

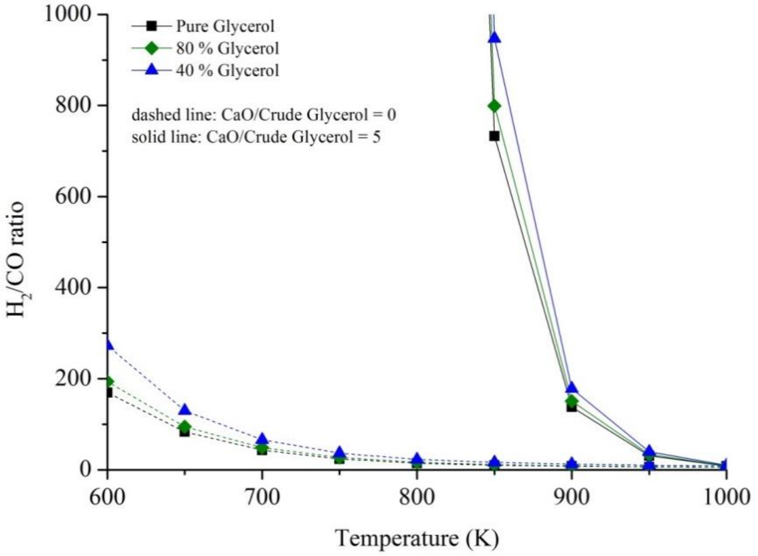

Figure 4.16. Autothermal reforming process with and without CO_2 sorption, at WCGFR = 9, OCGFR = 0.4 and 1 atm; effect of temperature and glycerol crude composition on H_2/CO ratio.

In order to optimize the sorption process, a study was made to find the minimum amount of adsorbent (calcium oxide) needed to maximize the yield of hydrogen in the thermodynamic equilibrium. Figure 4.17 describes the hydrogen yield behaviour as a function of CaO to crude glycerol ratio for three different crude compositions. Comparing Figures 4.17 (a) and (b), one can observe that the higher the temperature, the lower is the CaO content needed to maximize the hydrogen yield. However, at 1000 K the maximum yield of hydrogen is lower than at 800 K. This can be explained by the exothermicity of reactions 2.22 and 2.23. At 1000 K, these reactions are inhibited so there is some carbon dioxide that is no longer adsorbed and remains in the system even if there are enormous quantities of adsorbent fed. Figures 4.17 (c) and (d) demonstrate that the water and oxygen content in the feed does not influence the amount of adsorbent required to maximize the yield of hydrogen.

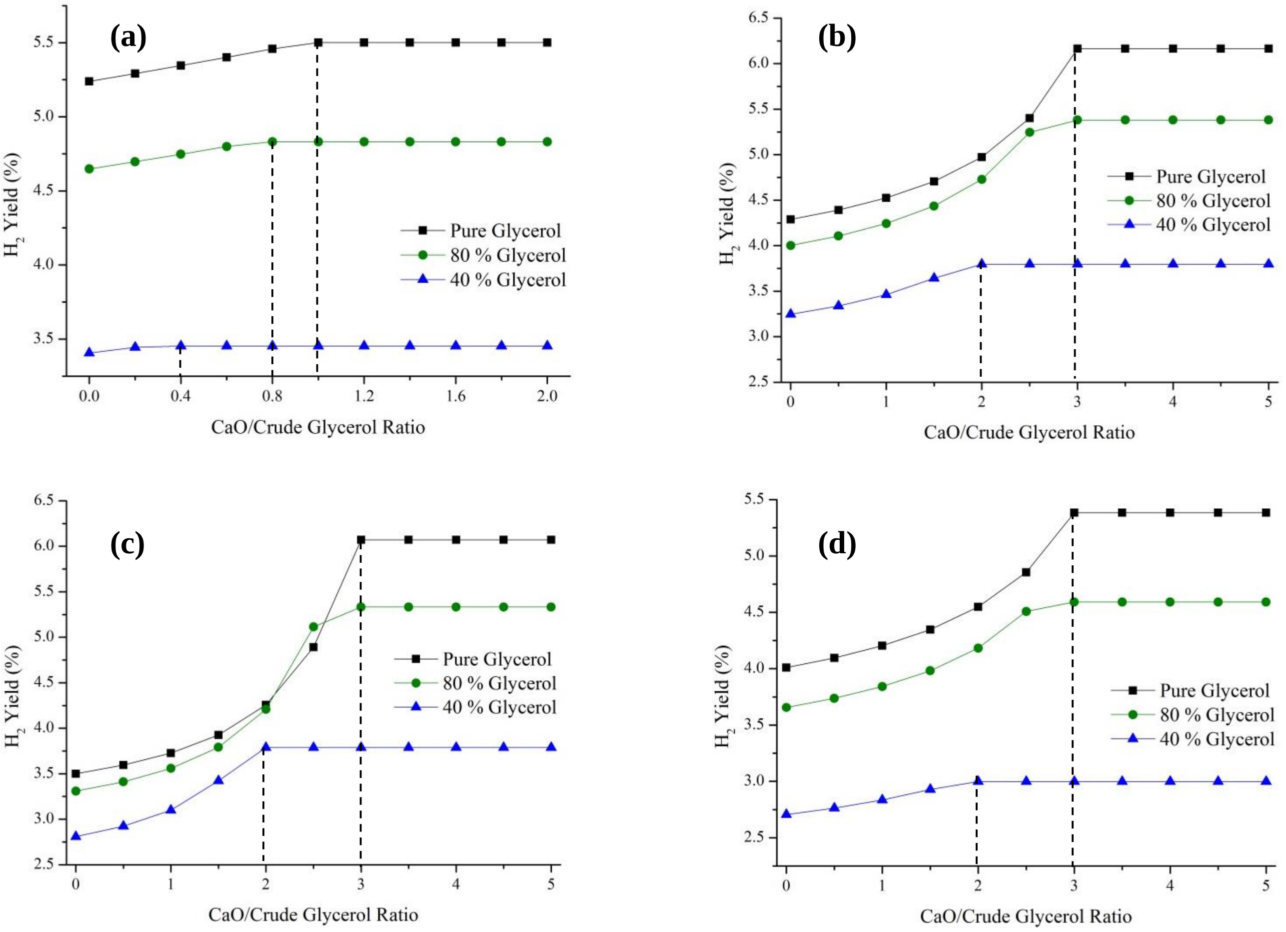

Figure 4.17. Hydrogen yield as a function of calcium oxide to crude ratio for the autothermal reforming process at: (a) atmospheric pressure, 1000 K, 0.4 OCGFR and 9 WCGFR; (b) atmospheric pressure, 800 K, 0.4 OCGFR and 9 WCGFR; (c) atmospheric pressure, 800 K, 0.4 OCGFR and 6 WCGFR; (d) atmospheric pressure, 800 K, 0.8 OCGFR and 9 WCGFR.

4.2.5 Autothermal reforming with simultaneous H_2 separation and CO_2 sorption – Effect of temperature and glycerol crude composition

The effect of both CO_2 sorption and H_2 separation (which could be reached in a hybrid multifunctional sorption-enhanced membrane reactor) as a function of the temperature is illustrated in Figure 4.18. One can observe that hydrogen yield is nearly constant until ca. 900 K (then slightly decreases) and there is no methane in the reaction equilibrium mixture (over the entire temperature range studied) when CO_2 is adsorbed on calcium oxide and H_2 is separated e.g. by a Pd-based membrane (Figure 4.18 (a) and (d)). This behaviour indicates that methanation is completely inhibited at these conditions. Furthermore, there is neither CO nor CO_2 in the equilibrium system up to 850 K and 800 K, respectively. The main advantage of simultaneously removing H_2 and CO_2 from the reaction medium is that it is possible to reach the maximum hydrogen yield at a temperature as low as 600 K. Moreover, no by-products are present (even in the retentate stream) apart from steam.

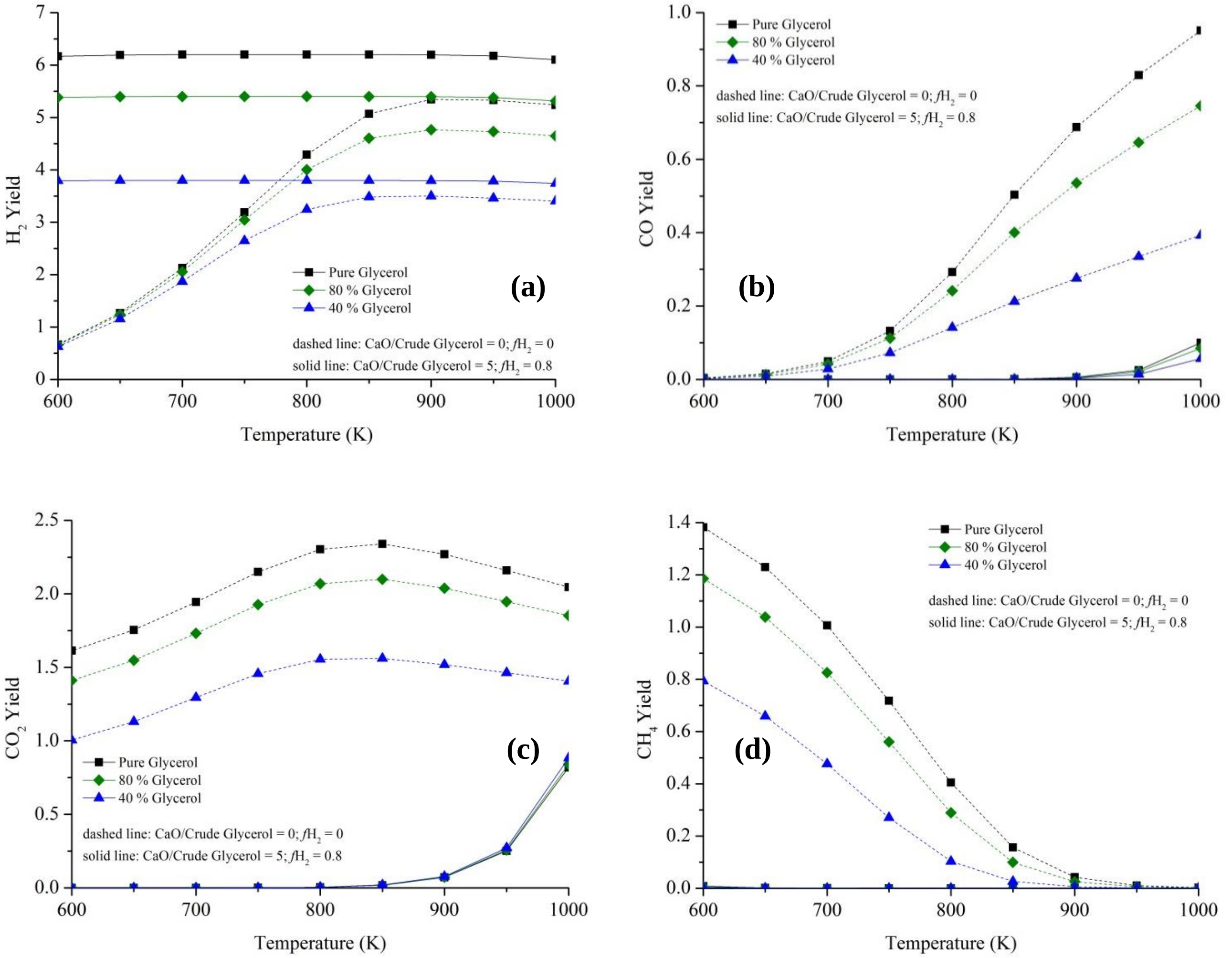

Figure 4.18. Effect of temperature and glycerol crude composition on the yield of (a) hydrogen, (b) carbon monoxide, (c) carbon dioxide and (d) methane for the autothermal refoming process with H_2 separation and CO_2 sorption, at WGFR=9, OGCFR=0.4 and 1 atm.

The effect of CO_2 sorption and H_2 separation on hydrogen purity in the retentate stream (dry basis) as a function of temperature is depicted in Figure 4.19. The maximum purity of hydrogen at the thermodynamic equilibrium in a traditional reactor (without CO_2 sorption nor H_2 separation) is approximately 66 % and it can be obtained from 900 K on. As one can see, hydrogen purity drops considerably for the ATR process with 'in situ' separation of hydrogen. This is expected once in the figure is shown the retentate stream, while there is pure hydrogen leaving the reaction medium to the permeate side of the membrane reactor. On the other hand, hydrogen purity may reach 99.94 % in the retentate stream when there is both CO_2 sorption on CaO and H_2 removal by a selective membrane; in such conditions, two highly pure hydrogen streams are obtained in a wide temperature range.

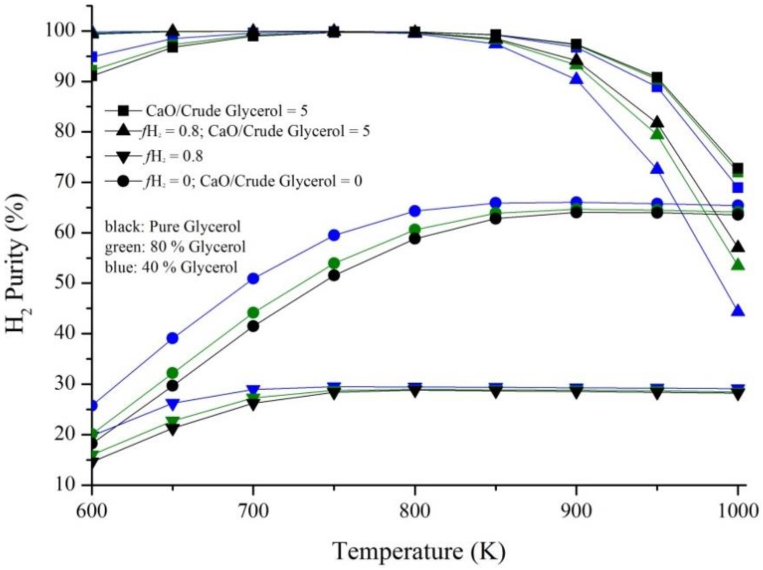

Figure 4.19. Effect of CO_2 sorption and H_2 separation on hydrogen purity in the retentate stream as a function of temperature.

4.2.6. Energetically neutral conditions

In an autothermal reforming process, oxygen is fed in the system in order to supply the heat required for endothermic reforming reactions, which is generated by oxidation of glycerol. The higher the oxygen to crude glycerol ratio is, the lower will be the heat requirement. Thus, it is possible to operate the reformer without supplying external heat by controlling the oxygen to crude glycerol ratio. The energetically neutral condition is the one at which the heat duty of the isothermal reformer equals zero.

Figure 4.20 shows the effect of inlet (feed) temperature on the oxygen to crude glycerol feed ratio (OCGFR) needed to supply the necessary heat for the steam reforming to be operated under energetically neutral conditions (null heat duty) when the reformer is operated at 800 K and the water to crude glycerol feed ratio (WCGFR) is 9. Increasing the inlet temperature leads to a reduction in the OCGFR and consequently the yield of hydrogen rises. This happens because when less oxygen is fed, less glycerol is partially oxidized, and therefore more glycerol is decomposed into hydrogen and carbon monoxide. As per stoichiometry, the decomposition of glycerol reaction (2.4) produces the same number of moles of hydrogen than the partial oxidation (2.13), but the later yields CO_2, thus favoring RWGS (eq. 2.5). At 350 K of inlet temperature, the OCGFR is considerably higher because at this temperature there is a big fraction of the feed that is still liquid (Appendix B, Table B.1). So, an even greater amount of oxygen is needed not only to provide the heat for the reformer to be operated at the desired temperature (800 K) but also to vaporize that liquid fraction. Figures 4.21 (a) and (b) depict the behavior of OCGFR required to achieve energetically neutral conditions as a function of inlet temperature for a membrane and a sorption-enhanced reformer, respectively, operating at 800 K and with a WCGFR of 9. The OCGFR and H_2 yield behaviors in a membrane and in a traditional reactor have the same trends (see Figures 4.20 and 4.21 (a)). The main differences between them are that a higher yield of hydrogen is achieved when hydrogen is separated from the reaction medium and the increase of hydrogen production with inlet temperature is more pronounced for the membrane reformer. On the other hand, completely different results were obtained for the case of a sorption-enhanced reformer.

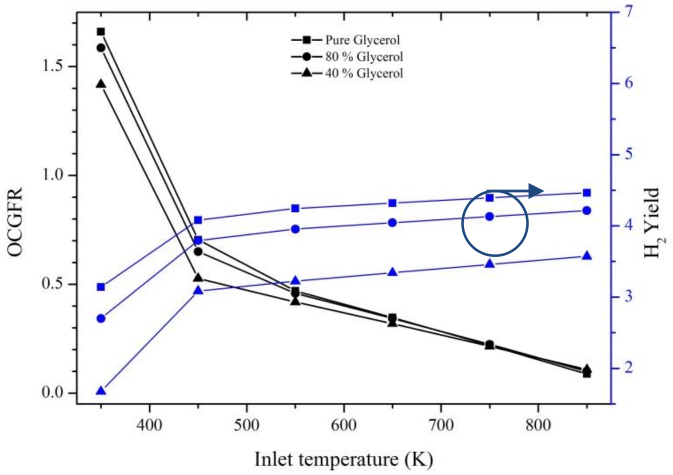

Figure 4.20. OCGFR needed to achieve energetically neutral conditions and H_2 yield in thermodynamic equilibrium as a function of inlet temperature at T = 800 K and WCGFR = 9 for three different crudes (traditional reformer).

Except for a temperature of 350 K (where there is a higher fraction of liquid), no oxygen is needed to provide heat for the steam reforming in the sorption-enhanced reactor (Fig. 4.21 (b)). This can be explained by the exothermicity of CO_2 sorption reactions (2.22) and (2.23). In fact, the heat released by these reactions is more than enough to maintain the autothermal reformer at 800 K when the CaO/Crude Glycerol feed ratio is 3. This cannot be observed in Figure 4.21 (b) because it only represents the OCGFR needed to achieve energetically neutral conditions but it can be verified from the analysis of Figure 4.22. Therefore, the sorption-enhanced reforming of glycerol can be an autothermal process even without oxidation reactions.

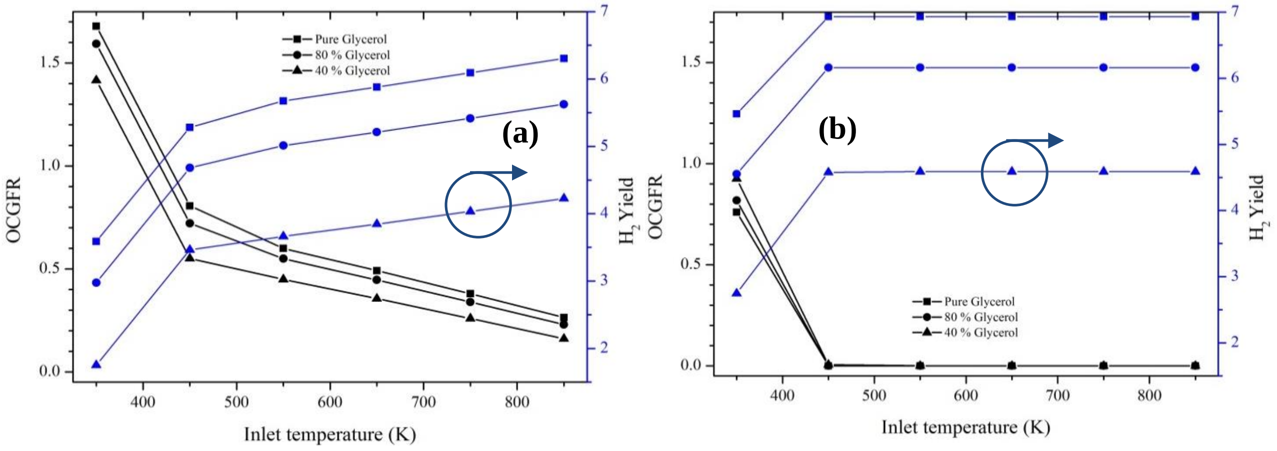

Figure 4.21. OCGFR needed to achieve energetically neutral conditions and H_2 yield in thermodynamic equilibrium as a function of inlet temperature at T = 800 K and WCGFR = 9 for three different crudes. (a) membrane reformer with $fH_2 = 0.8$ (b) sorption-enhanced reformer with CaO/Crude Glycerol = 3.

Figure 4.22 depicts the calcium oxide to crude glycerol ratio necessary to reach energetically neutral conditions as a function of inlet temperature for the glycerol sorption-enhanced reforming process. Although the CaO/Crude Glycerol ratio that gives the maximum hydrogen yield on a sorption-enhanced reformer at 800 K is 3 (see figure 4.17 (b)), a lesser amount of adsorbent is enough to supply the required heat for the reforming reactions. Any point above the curves of CaO/Crude Glycerol vs Inlet Temperature indicate that there is an excess of heat generation in the reformer that must be removed in order to maintain the desired temperature inside the reactor. Moreover, the CaO/Crude Glycerol ratio required decreases with the increase of inlet temperature and consequently the yield of hydrogen at thermodynamic equilibrium also decreases. Figures 4.23 represent the adsorbent to crude glycerol feed ratio necessary to achieve energetically neutral conditions and the hydrogen yield at thermodynamic equilibrium as a function of inlet temperature in an isothermal sorption-enhanced membrane reformer with hydrogen separation fraction of 0.8. From its analysis it is possible to observe that a greater amount of calcium oxide is needed to achieve energetically neutral conditions when hydrogen is separated from the reaction medium.

This is a result of the prominent inhibition of the exothermic methanation reaction represented by equation 2.6, as described above. If there is less methane being produced due to the lack of hydrogen in the medium, there will be less heat released by this reaction and consequently more sorbent is needed to achieve energetically neutral conditions through reactions 2.22 and 2.23 (Table 2.2).

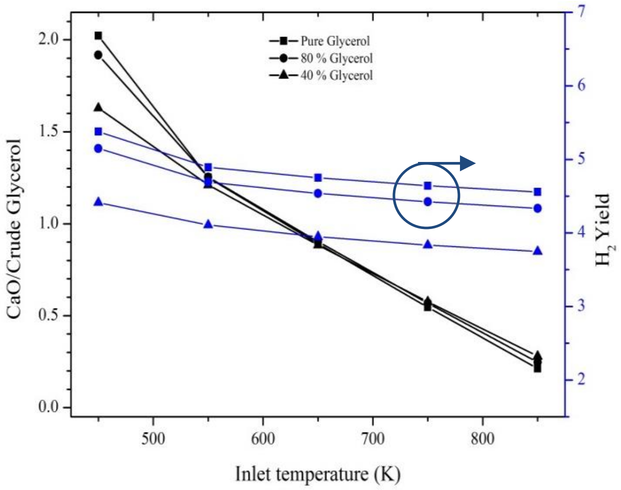

Figure 4.22. CaO/Crude Glycerol needed to achieve energetically neutral conditions and H_2 yield in thermodynamic equilibrium as a function of inlet temperature at T = 800 K and WCGFR = 9 for three different crudes (sorption-enhanced reformer).

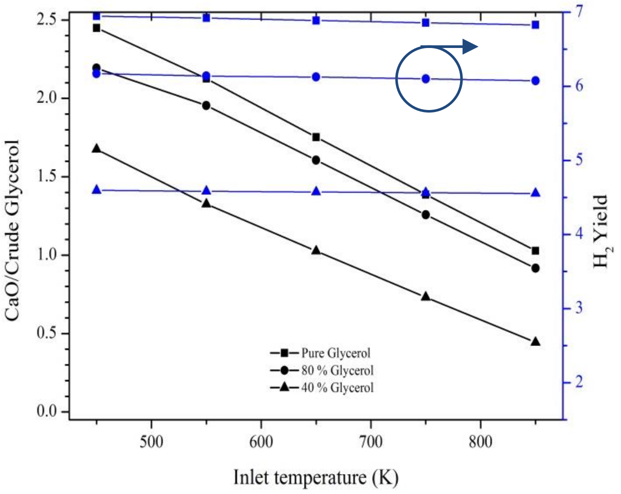

Figure 4.23. CaO/Crude Glycerol needed to achieve energetically neutral conditions and H_2 yield in thermodynamic equilibrium as a function of inlet temperature at T = 800 K and WCGFR = 9 for three different crudes (sorption-enhanced membrane reformer with fH_2 = 0.8)

Table 4.4 presents the optimal operating conditions of crude glycerol steam autothermal reforming with and without in situ H_2 separation at energetically neutral conditions. In a traditional reactor, the maximum hydrogen yield (4.79) is attained at 900 K, water to crude glycerol feed ratio (WCGFR) of 9 and oxygen to crude glycerol feed ratio (OCGFR) of 0.76 for a pure glycerol crude. On the other hand, the maximum hydrogen purity (64.2 mol. %) is achieved at 800 K and OCGFR of 0.42 for a glycerol content of 40 % in the crude. In a membrane reactor with a hydrogen separation factor of 0.8, the maximum yield (5.68) is attained at 900 K and OCGFR of 0.6 for pure glycerol crude, whereas the maximum hydrogen purity (29.6 vol. %) is achieved at 700 K and OCGFR of 0.33 for a glycerol content of 40 % in the crude. The hydrogen purity in a membrane reactor (in the retentate side) is substantially lower than in a traditional reactor because hydrogen is being selectively separated from the reaction medium.

Table 4.4. Optimal operating conditions of crude glycerol autothermal reforming with and without H_2 in situ separation at energetically neutral conditions (Inlet temperature = 550 K).

	Glycerol content (%)	Temperature (K)	WCGFR	OCGFR	H_2 Yield	H_2 Purity* (mol. %) (dry basis)
ATR traditional reactor	100	700	9	0.03	2.18	42.1
		800		0.47	4.24	58.6
		900		0.76	**4.79**	61.5
	80	700		0.06	2.12	44.9
		800		0.46	3.96	60.3
		900		0.69	4.28	62.2
	40	700		0.12	1.96	52.1
		800		0.42	3.22	**64.2**
		900		0.57	3.19	64.0
ATR membrane reactor (fH_2 = 0.8)	100	700		0.40	5.49	26.2
		800		0.60	**5.68**	27.4
		900		0.73	5.36	26.3
	80	700		0.38	5.00	27.3
		800		0.55	5.01	27.8
		900		0.67	4.72	26.7
	40	700		0.33	3.79	**29.6**
		800		0.45	3.66	28.9
		900		0.56	3.42	27.5

* In the retentate stream for ATR membrane reactor.

Table 4.5 presents the optimal operating conditions of crude glycerol sorption-enhanced steam autothermal reforming with and without in situ H_2 separation at energetically neutral conditions. In a sorption-enhanced reactor, the maximum yield (6.60) is attained at 900 K, WCGFR of 9 and sorbent to crude glycerol feed ratio of 2.21 for pure glycerol. On the other hand, the maximum hydrogen purity (97.5 mol. %) is achieved at 900 K and CaO/Crude Glycerol of 1.68 for a glycerol content of 40 % in the crude. In a sorption-enhanced membrane reactor with a hydrogen separation factor of 0.8, the maximum yield (6.93) is attained at 900 K and CaO/Crude Glycerol of 2.23 for pure glycerol, whereas the maximum hydrogen purity (90.7 mol. %) is achieved at 900 K and CaO/Crude Glycerol of 1.71 for a glycerol content of 40 % in the crude.

4.3. Dry autothermal reforming

In this section a complementary study of the dry autothermal reforming (DATR) process is reported. Unlike the steam autothermal reforming process section, this one does not include the study of in situ CO_2 sorption. This study was not performed once CO_2 is one of the reactants in this

Table 4.5. Optimal operating conditions of crude glycerol sorption–enhanced autothermal reforming with and without H_2 in situ separation at energetically neutral conditions (Inlet temperature = 550 K).

	Glycerol content (%)	Temperature (K)	WCGFR	CaO/Crude Glycerol	H_2 Yield	H_2 Purity* (mol. %) (dry basis)
Sorption-enhanced reactor	100	700	9	0.08	2.20	43.0
		800		1.25	4.89	73.7
		900		2.21	**6.60**	89.4
	80	700		0.16	2.17	47.1
		800		1.25	4.69	77.7
		900		2.05	5.97	91.6
	40	700		0.32	2.10	58.7
		800		1.21	4.11	87.5
		900		1.68	4.57	**97.5**
Sorption-enhanced membrane reactor (fH_2 = 0.8)	100	700		1.05	5.83	37.4
		800		1.76	6.89	52.7
		900		2.23	**6.93**	64.4
	80	700		1.04	5.45	41.1
		800		1.62	6.14	55.6
		900		2.05	6.16	69.3
	40	700		0.94	4.41	50.5
		800		1.33	4.58	65.9
		900		1.71	4.60	**90.7**

* In the retentate stream for sorption-enhanced membrane reactor.

process, being fed into the reformer in order to be converted into CO and H_2O through RWGS reaction.

Beyond syngas production, the main interest of DATR is to convert and use CO_2 as raw material. In addition to the study performed in section 4.1.1, a simulation of dry and dry autothermal reforming with H_2 separation was performed and the results are reported in section 4.3.1. Furthermore, a succinct investigation of the energetically neutral conditions of dry autothermal reforming (DATR) of crude glycerol is reported in subsection 4.3.2.

4.3.1 Dry autothermal reforming with H_2 separation

Instead of being converted, carbon monoxide is produced in DATR process. Moreover, the in situ removal of hydrogen causes an increase on carbon dioxide formation in the DATR, as one can observe in Table 4.6, which depicts the CO_2 conversion at 1000 K (temperature at which maximum hydrogen yield is achieved) for three different crudes with and without H_2 separation for DATR and DR processes . H_2 removal limits the CO_2 conversion by favoring not the RWGS but the WGS reaction. On the other hand, more syngas with a higher H_2/CO ratio is produced when H_2 is separated, but the difference is not significant tough. Another drawback of using a selective membrane to separate H_2 from the reaction medium in a DATR or DR process is that palladium membranes, which are the most used for hydrogen separation, can only be operated at temperatures between 573 and 873 K [27].

Furthermore, it can be also observed that the higher the glycerol content in the crude, the lower is the conversion of carbon dioxide. This is a result of the higher amount of carbon monoxide that is produced by decomposition of glycerol compared to the number of moles produced by decomposition of methanol (cf. Tables 2.2 and 2.3). The presence of carbon monoxide in the equilibrium limits the RWGS and consequently the CO_2 conversion drops.

Table 4.6. CO_2 conversion and H_2 yield for crude glycerol dry reforming with and without hydrogen separation at 1000 K, CCGFR = 1 and 1 atm.

	Glycerol content (%)	CO_2 conversion (%)	H_2 Yield			Syngas Yield	H_2/CO ratio
			Retentate	Permeate (pure H_2)	Total		
DR traditional reactor	100	27.0			3.22	6.22	1.07
	80	32.4			2.89	5.65	1.05
	40	38.1			2.22	4.33	1.05
DR membrane reactor (fH_2 = 0.8)	100	-0.9	0.76	3.03	3.79	6.58	1.36
	80	6.9	0.68	2.73	3.41	5.98	1.33
	40	15.2	0.53	2.11	2.64	4.58	1.35
DATR traditional reactor	100	-28			2.95	5.63	1.10
	80	-26			2.57	2.88	1.11
	40	-23			1.80	3.36	1.15
DATR membrane reactor (fH_2 = 0.8)	100	-80	0.72	2.87	3.59	5.79	1.63
	80	-78	0.64	2.53	3.17	4.99	1.74
	40	-71	0.46	1.84	2.30	3.39	2.11

4.3.2 Dry autothermal reforming – Energetically neutral conditions

As with steam autothermal, the dry autothermal process includes oxygen in the feed in order to supply the heat required for endothermic reforming reactions, which is generated by oxidation of glycerol or methanol.

From Figure 4.23, it is possible to observe that the oxygen requirement is lower when the inlet temperature is higher. The higher the inlet temperature, the lower the required heat to maintain the

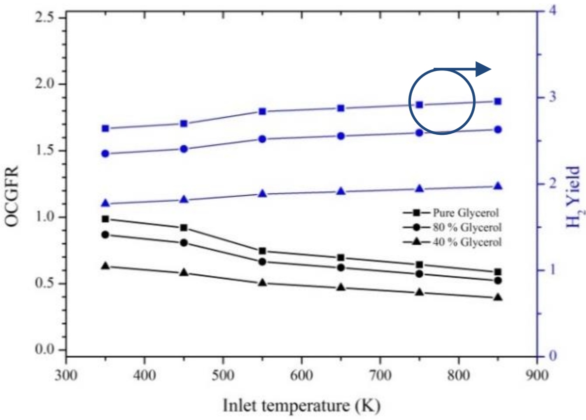

Figure 4.24. OCGFR needed to achieve energetically neutral conditions and H_2 yield in thermodynamic equilibrium as a function of inlet temperature for DATR process at T = 1000 K and CCGFR = 1 for three different crudes.

isothermal reformer at 1000 K. Moreover, the necessary OGFR to achieve energetically neutral conditions is lower when there is more methanol in the crude. This behavior is observed because the decomposition of methanol reaction (2.25) is less endothermic than the decomposition of glycerol (eq. 2.4).

Table 4.7 presents the optimal operating conditions of crude glycerol dry autothermal reforming at energetically neutral conditions. In a traditional reactor, the maximum yield of syngas is attained at 1000 K, CCGFR of 1 and oxygen to crude glycerol feed ratio of 0.75 for a pure glycerol crude. At these conditions, 5.38 moles of syngas are produced per mole of glycerol, with a H_2/CO ratio of 1.12.

Table 4.7. Optimal operating conditions of crude glycerol dry autothermal reforming at energetically neutral conditions (Inlet temperature = 550 K).

	Glycerol content (%)	Temperature (K)	CCGFR	OCGFR	Syngas Yield	H_2/CO ratio
DATR traditional reactor	100	800	1	-	-	-
		900		0.34	3.66	1.74
		1000		0.75	**5.38**	**1.12**
	80	800		-	-	-
		900		0.32	3.32	1.7
		1000		0.66	4.77	1.12
	40	800		-	-	-
		900		0.28	2.64	1.60
		1000		0.50	3.53	1.14

CHAPTER V – Conclusions and Future Work

6.1. Conclusions

A thermodynamic analysis of crude glycerol steam and dry autothermal reforming (ATR and DATR, respectively) processes has been performed to map the effects of different process variables on product distribution, particularly hydrogen and syngas yield.

Regarding ATR, the effects of pressure, temperature, oxygen to crude glycerol feed ratio (OCGFR), water to crude glycerol feed ratio (WCGFR), crude composition, in situ H_2 separation and in situ CO_2 sorption were studied. The atmospheric pressure (lower one assessed) was found to be the most adequate operating pressure in this process. Temperature and WCGFR have a positive effect on hydrogen yield; however the impact of oxygen content in the feed presents an opposite trend. The results of the simulations also show that the use of crude glycerol (i.e. impure glycerol, containing methanol) to produce hydrogen gives lower performance, compared to pure glycerol. On the other hand, the purity (dry basis) of hydrogen slightly increases with methanol content in the crude. The in situ separation of H_2 (e.g. through a perm-selective membrane) enhances the hydrogen and CO_2 production while inhibiting CO and CH_4 formation. Furthermore, the maximum hydrogen yield can be achieved at lower temperatures in a membrane reformer, compared to a traditional one. The in situ CO_2 sorption (e.g. in a sorption-enhanced reactor, coupling the carbon dioxide sorbent with the catalyst) has a similar effect on hydrogen, carbon monoxide and methane yields and can additionally remove carbon dioxide from the hydrogen rich output stream, thus improving process performance.

Considering the crude glycerol autothermal reforming in a traditional reactor at an energetically neutral condition (i.e., where no external heat input is required), a maximum hydrogen yield of 4.79 is attained at 900 K, WCGFR of 9 and OCGFR of 0.76 for pure glycerol at an inlet temperature of 550 K. In a membrane reactor with a hydrogen separation factor of 0.8, the maximum hydrogen yield obtained was 5.68, at 800 K, WCGFR of 9, OCGFR of 0.60 also for pure glycerol. The results of the simulations performed for glycerol autothermal reforming with in situ CO_2 separation revealed that no oxygen is needed to achieve energetically neutral conditions, due to the exothermic CO_2 sorption reactions. In a sorption-enhanced reactor, the maximum hydrogen yield at energetically neutral conditions is 6.60, which is attained at 900 K, WCGFR of 9 and CaO/Crude Glycerol of 2.21 for pure glycerol at an inlet temperature of 550 K. In a sorption-enhanced membrane reactor with a hydrogen separation factor of 0.8, a maximum yield of 6.93 (very close to the theoretical stoichiometric value of 7) is attained at 900 K and CaO/Crude Glycerol of 2.23 for pure glycerol.

Regarding DATR, the effects of pressure, temperature, OCGFR, CCGFR, crude composition and in situ H_2 separation were studied; because carbon dioxide is a reactant, ist capture by a selective sorbent was not considered. The study of the DATR shows that this process seems favorable for syngas production instead of pure hydrogen as it gives a H_2/CO ratio in the desirable range (~1). As seen in the ATR results, pressure, methanol content in the crude and oxygen content in the feed have a negative effect on both hydrogen and syngas production. Moreover, the CCGFR has a negligible effect on syngas production and a negative effect on hydrogen production, which makes this parameter good for adjusting the H_2/CO ratio to the desirable value (e.g. in the range between 1.33 and 0.73, for CCGFR between 0.5 and 3, at atmospheric pressure and 1000 K for pure glycerol), depending on its industrial end use. Hydrogen in situ removal was found to be a non-feasible solution for the dry reforming process because it limits the reverse water gas shift reaction, which converts CO_2 and hydrogen into CO and H_2O. Although the presence of oxygen inhibits CO_2 conversion, the DATR process is still attractive from the energetic point of view. In a traditional reactor, at a temperature of 1000 K, CCGFR of 1 and oxygen to crude glycerol feed ratio of 0.75 for pure glycerol, 5.38 moles of syngas were obtained per mole of glycerol with a H_2/CO ratio of 1.12, which was identified as the best energetically neutral condition for DATR operation.

6.2. Suggestions for future work

A few aspects, at least, can be the target of a future research. There are different types of CO_2 sorbents (e.g. hydrotalcite) under research that could be thermodynamically analyzed for the sorption-enhanced ATR in order to compare the effect of each one on equilibrium compositions. Besides methanol and glycerol, the crude is composed of other constituents (e.g. acetic acid [28]) whose influence on the performance of the processes could be also studied. Furthermore, it would be interesting to perform an economic balance of the different processes, with and without H_2 and/or CO_2 in situ-removal, to identify the most profitable one(s).

Finally, experimental tests would be helpful for comparing the theoretical results obtained in this thesis, as predicted from thermodynamic calculations, with real/experimentally obtained data.

CHAPTER VI – References

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Appendix A

The Soave- Redlich-Kwong equation of state is given by

$$P = \frac{RT}{v - b} - \frac{a\alpha(T)}{v(v + b)} \tag{A.1}$$

$$a\alpha(T) = 0.42748 \frac{R^2 T_C^2}{P_C \alpha(T)} \tag{A.2}$$

$$b = 0.08664 \frac{RT}{P_C} \tag{A.3}$$

$$\alpha(T) = [1 + m(1 - T_r^{0.5})]^2 \tag{A.4}$$

$$T_r = \frac{T}{T_C} \tag{A.5}$$

$$m = 0.480 + 1.574\omega - 0.176\omega^2 \tag{A.6}$$

where P is the gas pressure, P_C is the critical pressure, R is the ideal gas constant, T is temperature, T_r is the reduced temperature, T_c is the critical temperature, v is the molar volume, a is a constant that corrects for attractive potential of molecules, b is a constant that corrects for volume and ω is the acentric factor.

The fugacity coefficient, $\hat{\phi}_i$, can be calculated from the following expression:

$$ln\hat{\phi}_i = \frac{b_i}{b_m}(Z - 1) - ln\frac{P(v - b_m)}{RT} + \frac{a_m}{b_m RT}\left(\frac{b_i}{b_m} - \frac{2}{a_m}\sum_{k=1}^{N} y_k\, a_{ik}\right) ln\left(1 + \frac{b_m}{V}\right) \tag{A.7}$$

The mixture parameters in equation A.7 are defined by the mixture rules as following:

$$a_m = \sum_i \sum_k y_i y_k a_{ik} \tag{A.8}$$

$$b_m = \sum_i y_i b_i \tag{A.9}$$

$$\boldsymbol{a_{ik} = (a_i a_k)^{0.5}(1 - k_{ik})} \tag{A.10}$$

Appendix B

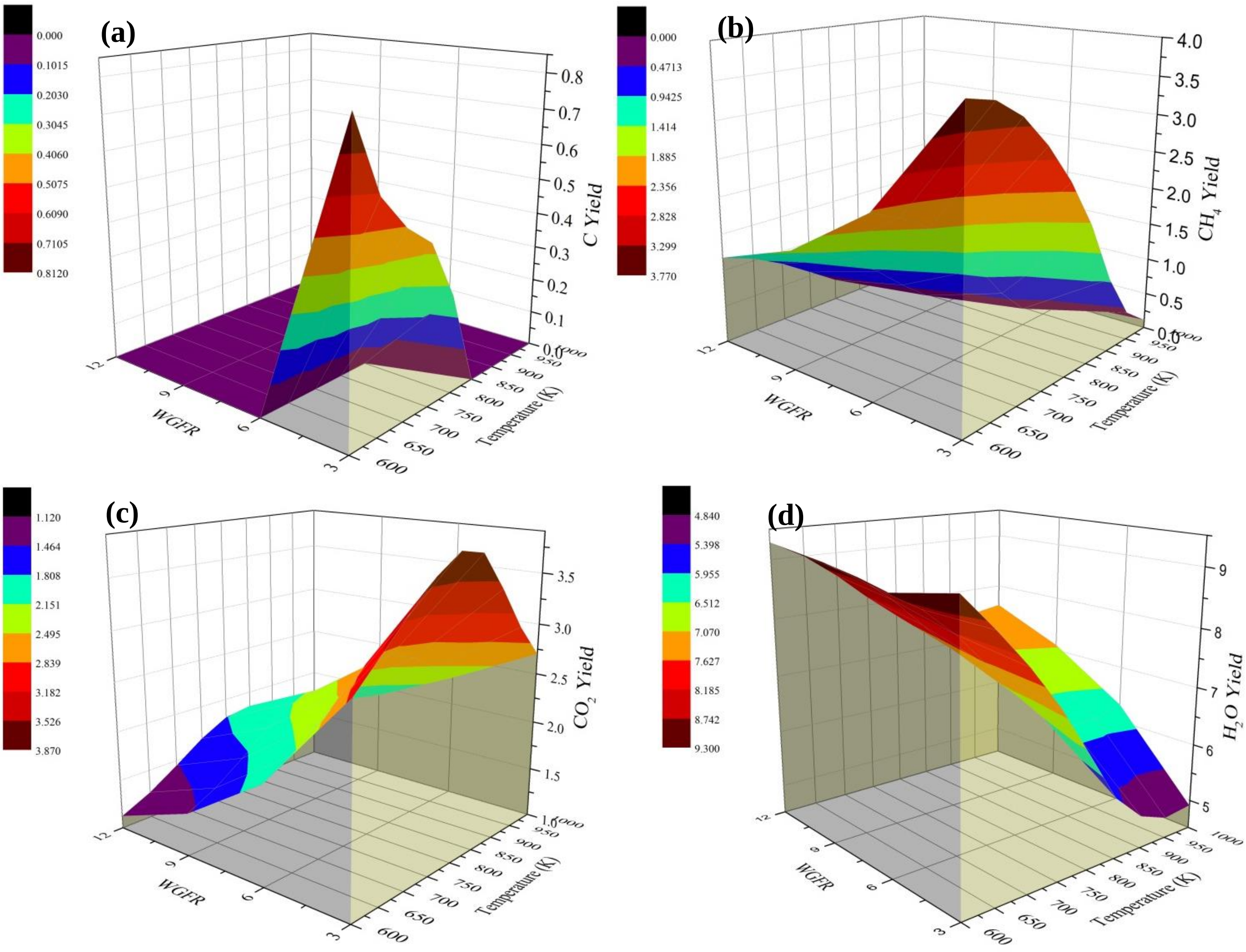

Figure B.1. Effect of WGFR and temperature on the yield of (a) solid carbon, (b) methane, (c) carbon dioxide and (d) water for the steam reforming of pure glycerol at atmospheric pressure.

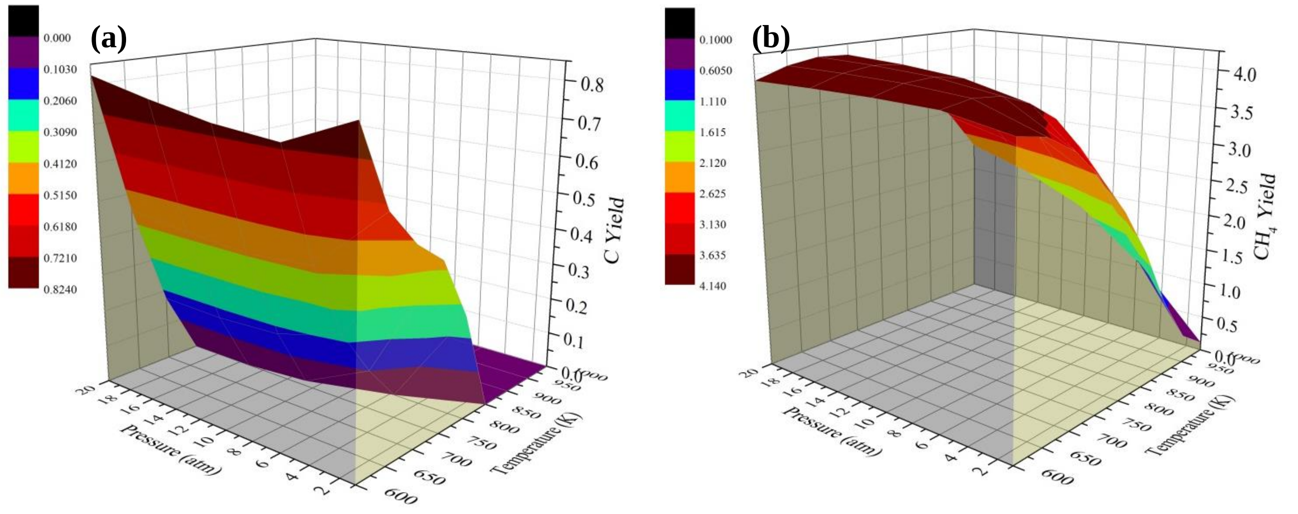

Figure B.2.1. Effect of pressure and temperature on the yield of (a) solid carbon and (b) methane for the steam reforming of pure glycerol at WGFR = 3.

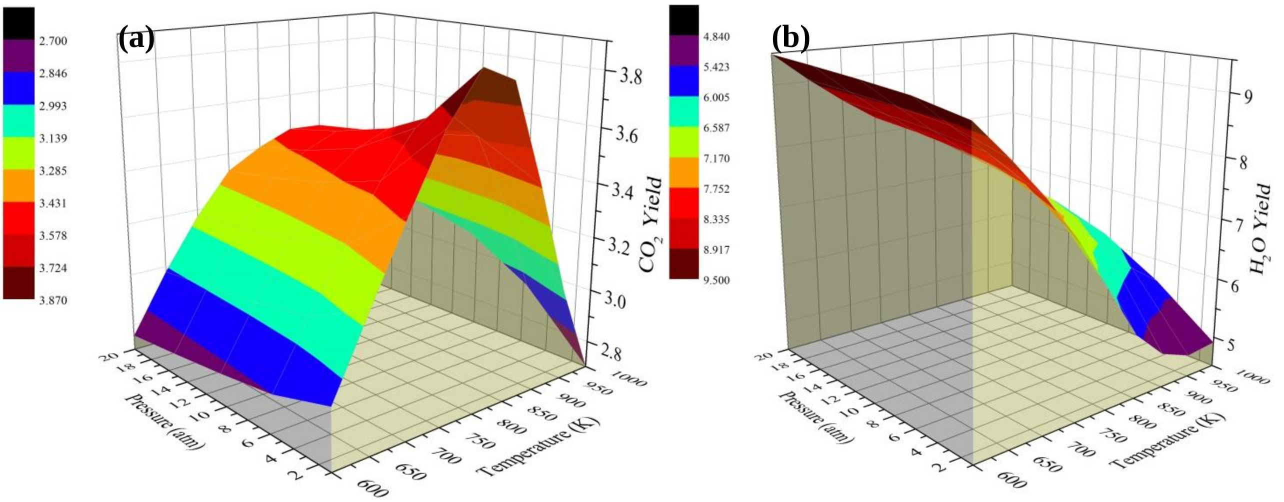

Figure B.2.2. Effect of pressure and temperature on the yield of (a) carbon dioxide and (b) water for the steam reforming of pure glycerol at WGFR = 3.

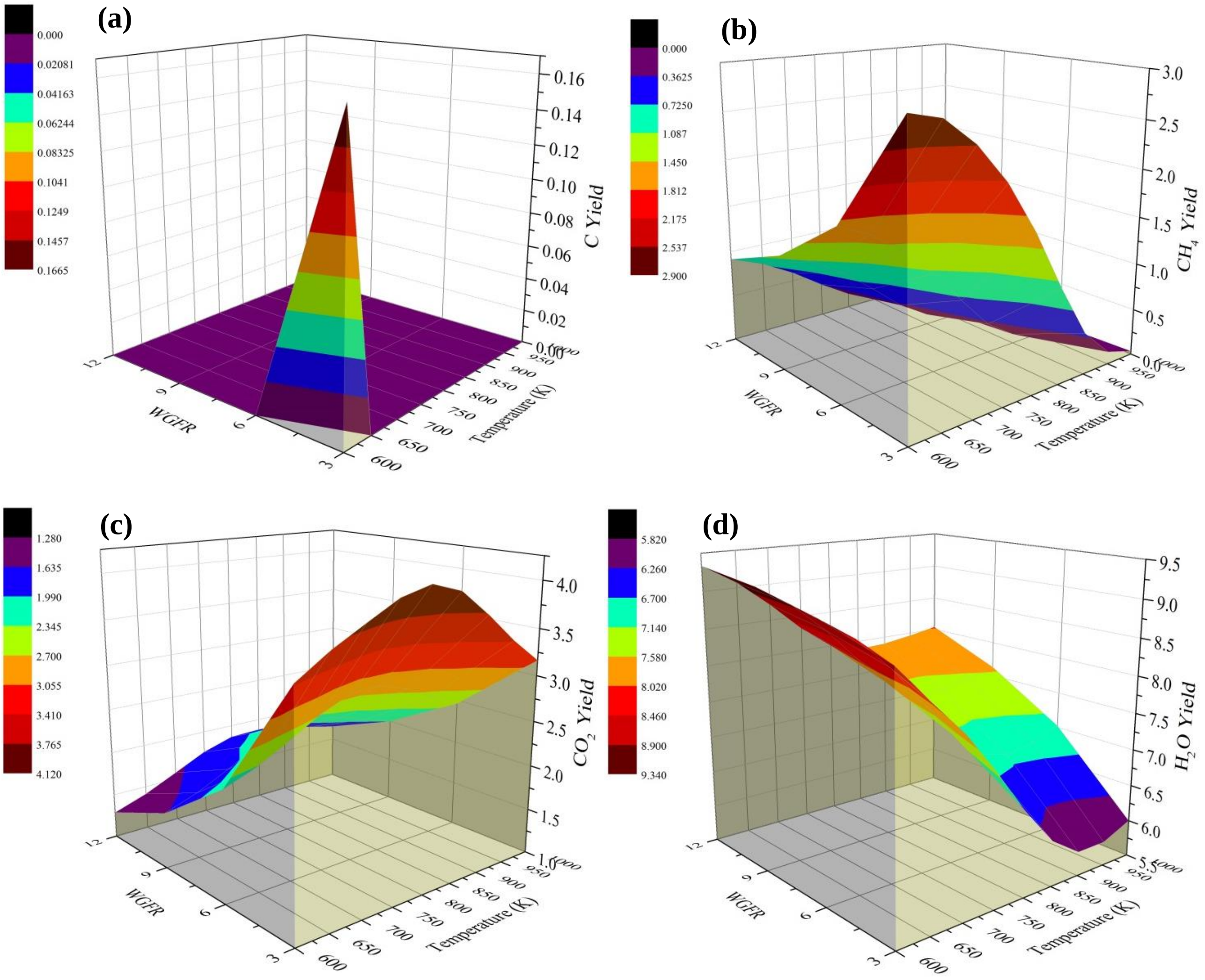

Figure B.3. Effect of WGFR and temperature on the yield of (a) solid carbon, (b) methane, (c) carbon dioxide and (d) water for the autothermal reforming of pure glycerol at atmospheric pressure and OGFR = 0.6.

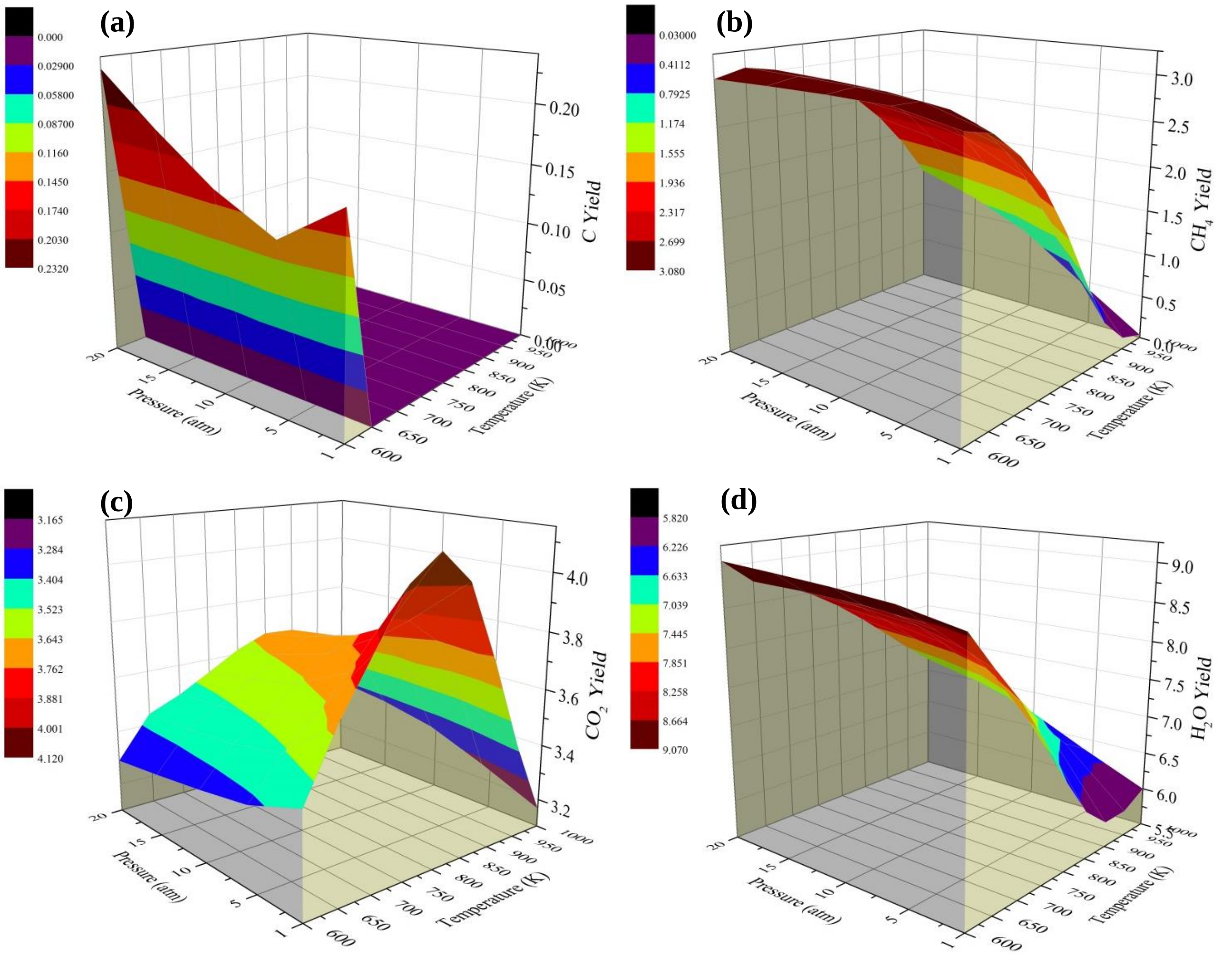

Figure B.4. Effect of pressure and temperature on the yield of (a) solid carbon, (b) methane, (c) carbon dioxide and (d) water for the autothermal reforming of pure glycerol at WGFR = 3 and OGFR = 0.6.

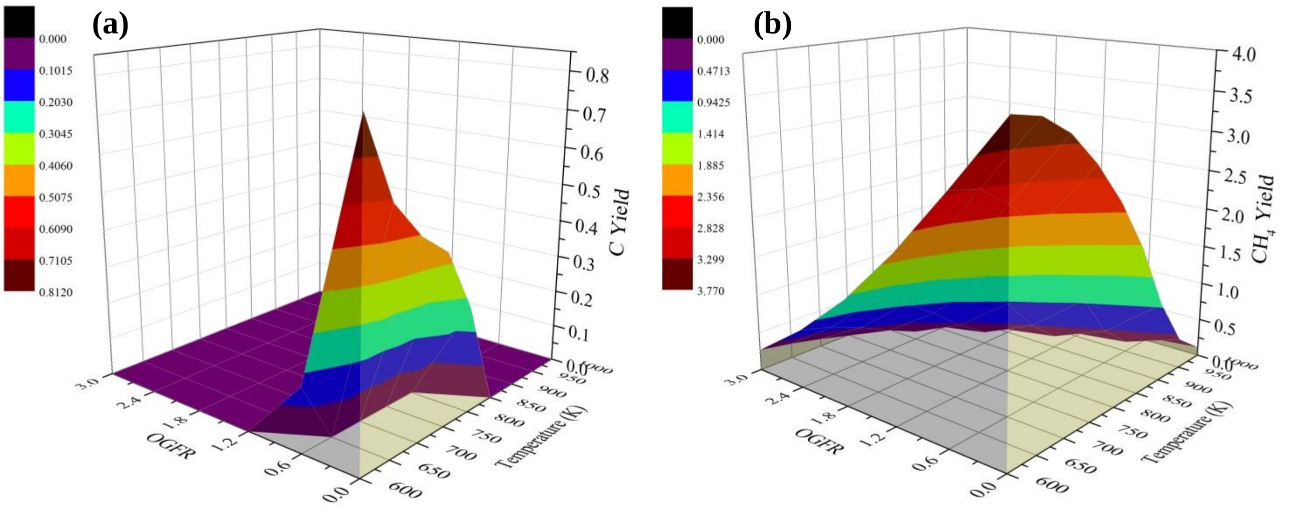

Figure B.5.1. Effect of OGFR and temperature on the yield of (a) solid carbon and (b) methane for the autothermal reforming of pure glycerol at atmospheric pressure and WGFR = 3.

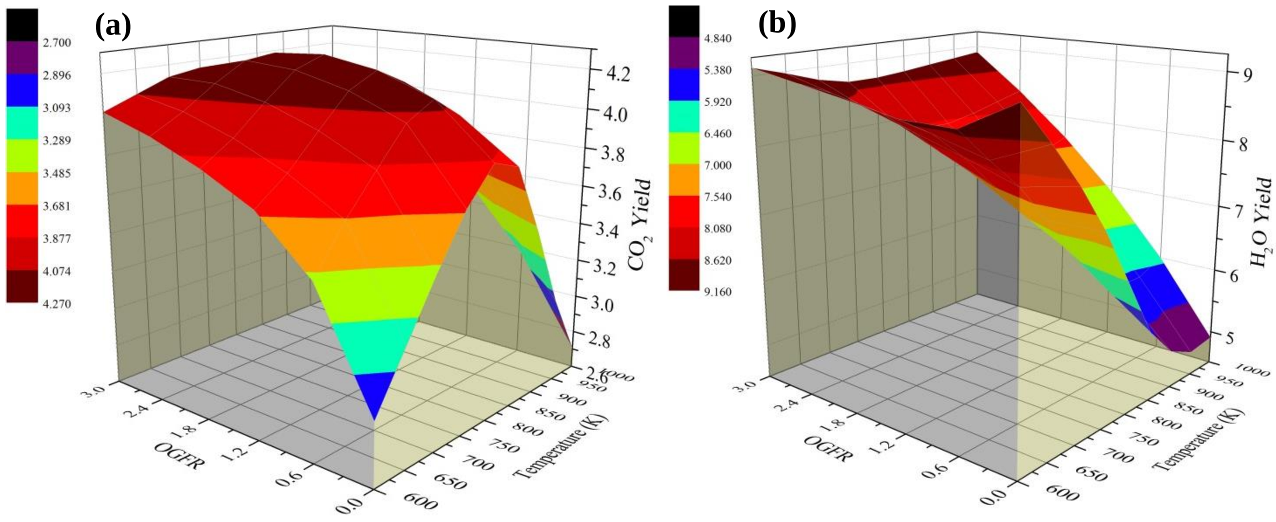

Figure B.5.2. Effect of OGFR and temperature on the yield of (a) carbon dioxide and (b) water for the autothermal reforming of pure glycerol at atmospheric pressure and WGFR = 3.

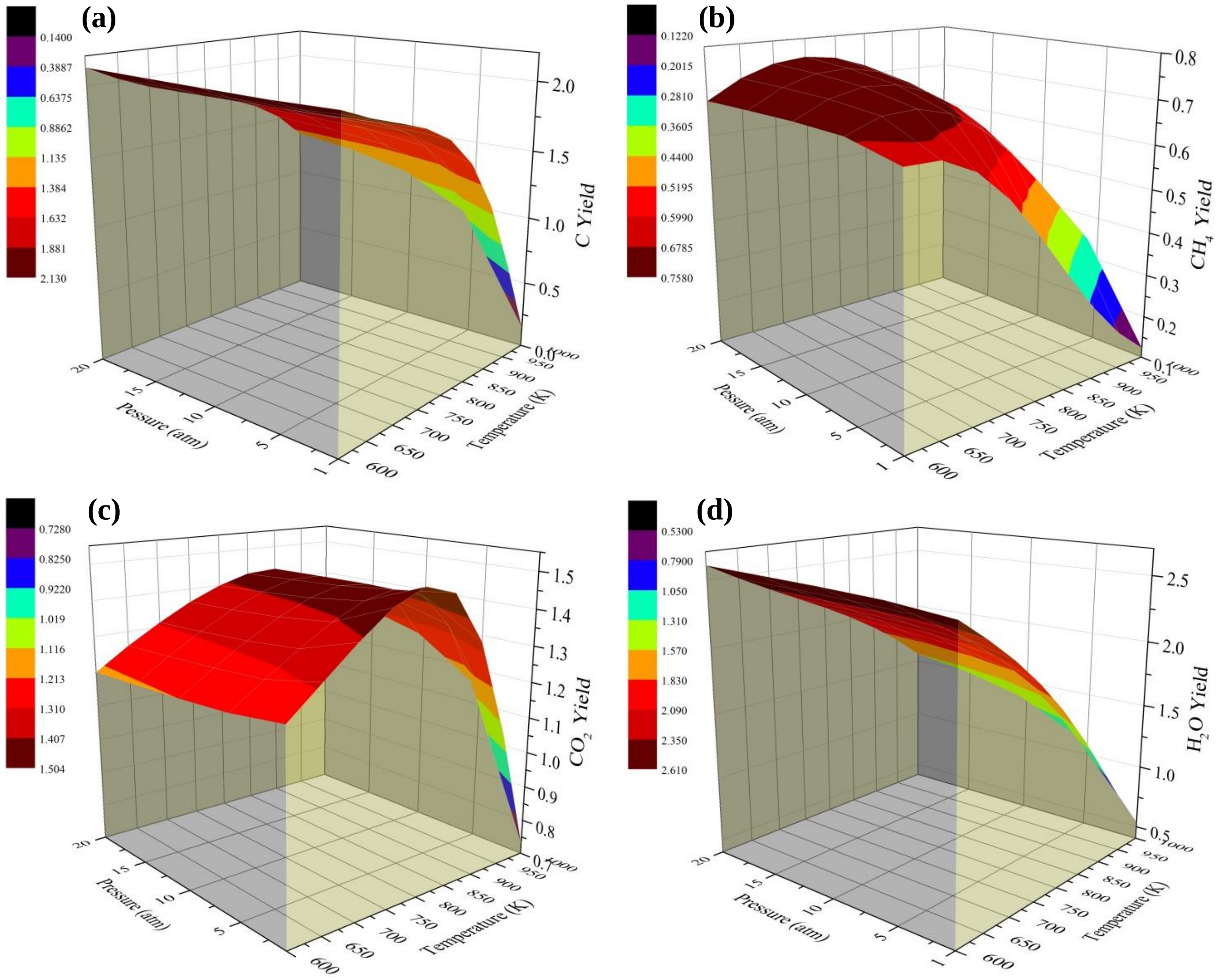

Figure B.6. Effect of pressure and temperature on the yield of (a) solid carbon, (b) methane, (c) carbon dioxide and (d) water for the dry reforming of pure glycerol at CGFR = 1.

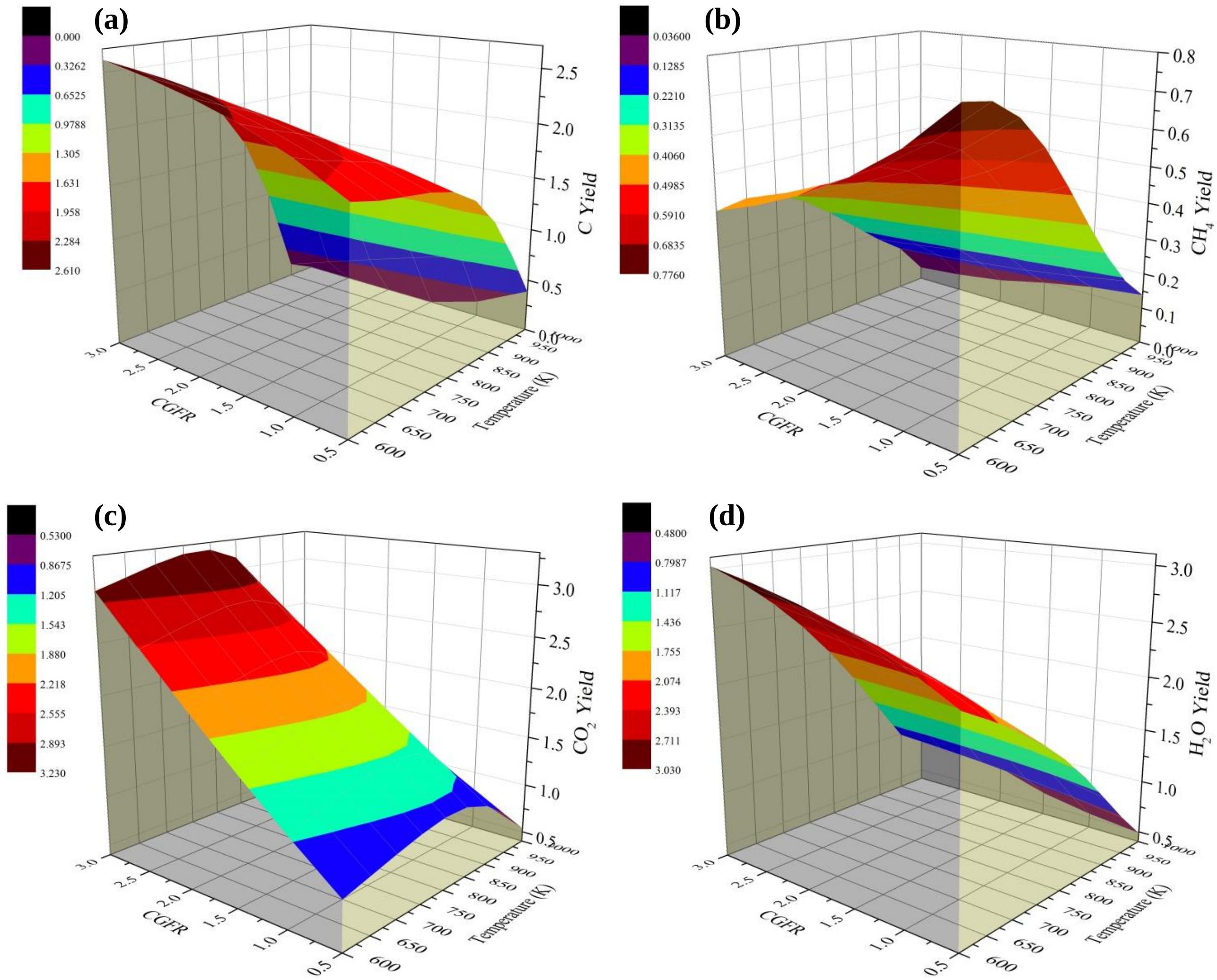

Figure B.7. Effect of CGFR and temperature on the yield of (a) solid carbon, (b) methane, (c) carbon dioxide and (d) water for the dry reforming of pure glycerol at atmospheric pressure.

Table B.1. Vapor fraction of the feed at different inlet temperatures for three different crudes.

Glycerol content in crude (%)	WCGFR	OCGFR	Inlet Temperature (K)	Vapor Fraction
100	9	1.66	350	0.22
		0.70	450	0.93
		0.47	550	1.00
80		1.59	350	0.23
		0.65	450	0.95
		0.46	550	1.00
40		1.42	350	0.26
		0.53	450	0.99
		0.42	550	1.00

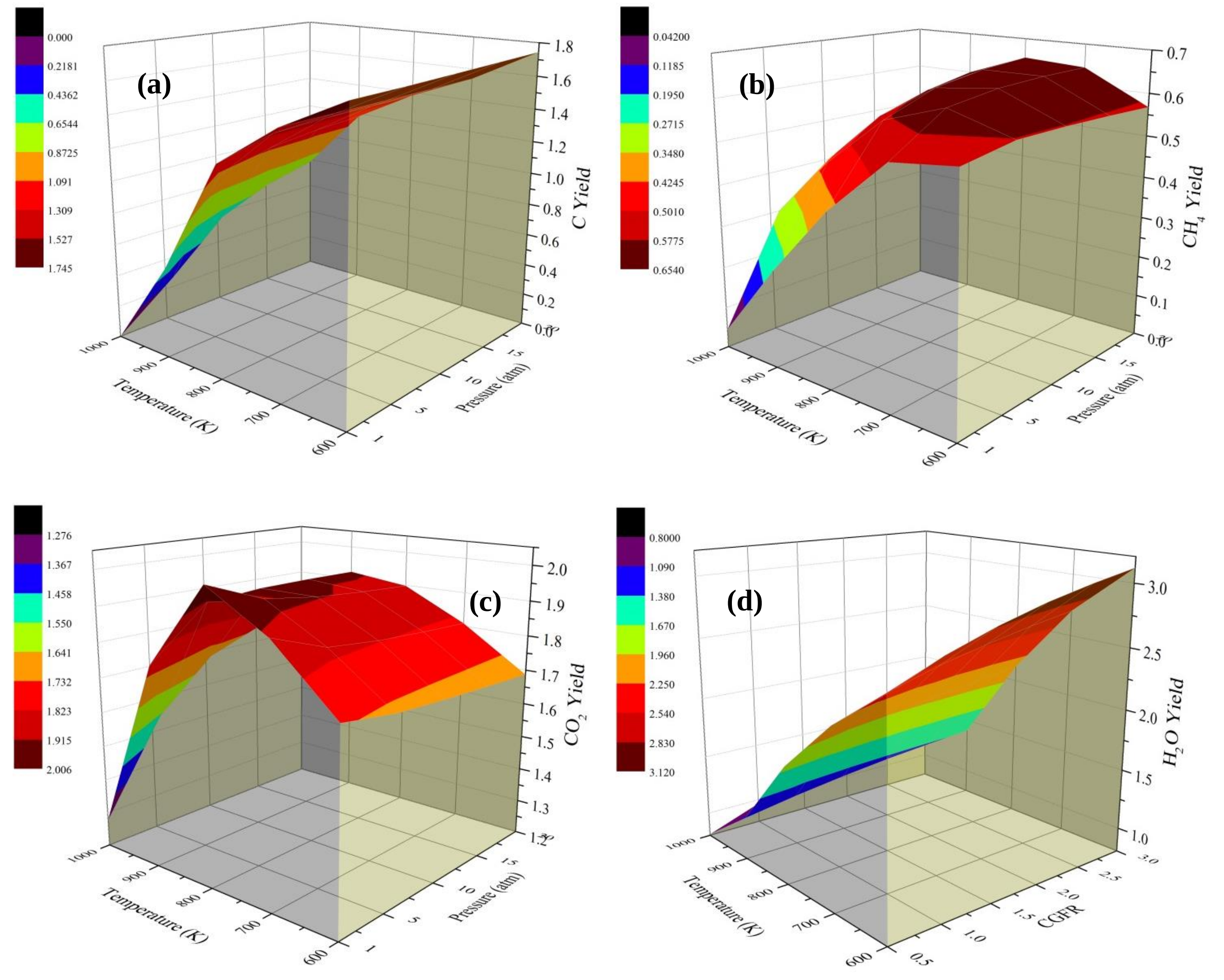

Figure B.8. Effect of pressure and temperature on the yield of (a) solid carbon, (b) methane, (c) carbon dioxide and (d) water for the dry autothermal reforming of pure glycerol at CGFR = 1 and OGFR = 0.6.

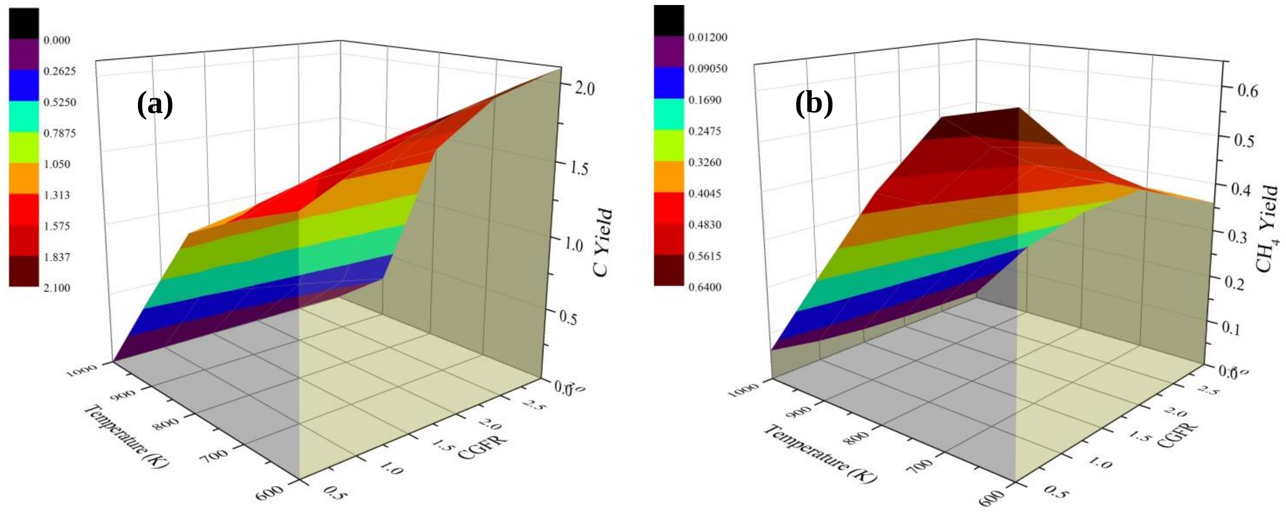

Figure B.9.1. Effect of temperature and CGFR on the yield of (a) solid carbon and (b) methane for the dry autothermal reforming of pure glycerol at atmospheric pressure and OGFR = 0.6.

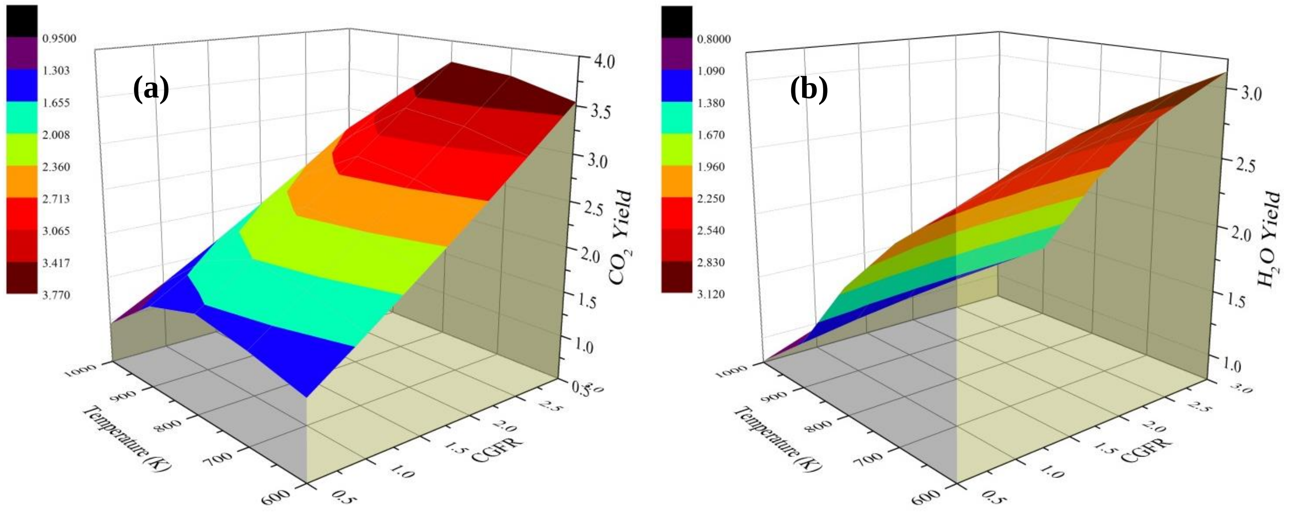

Figure B.9.2. Effect of temperature and CGFR on the yield of (a) carbon dioxide and (b) water for the dry autothermal reforming of pure glycerol at atmospheric pressure and OGFR = 0.6.

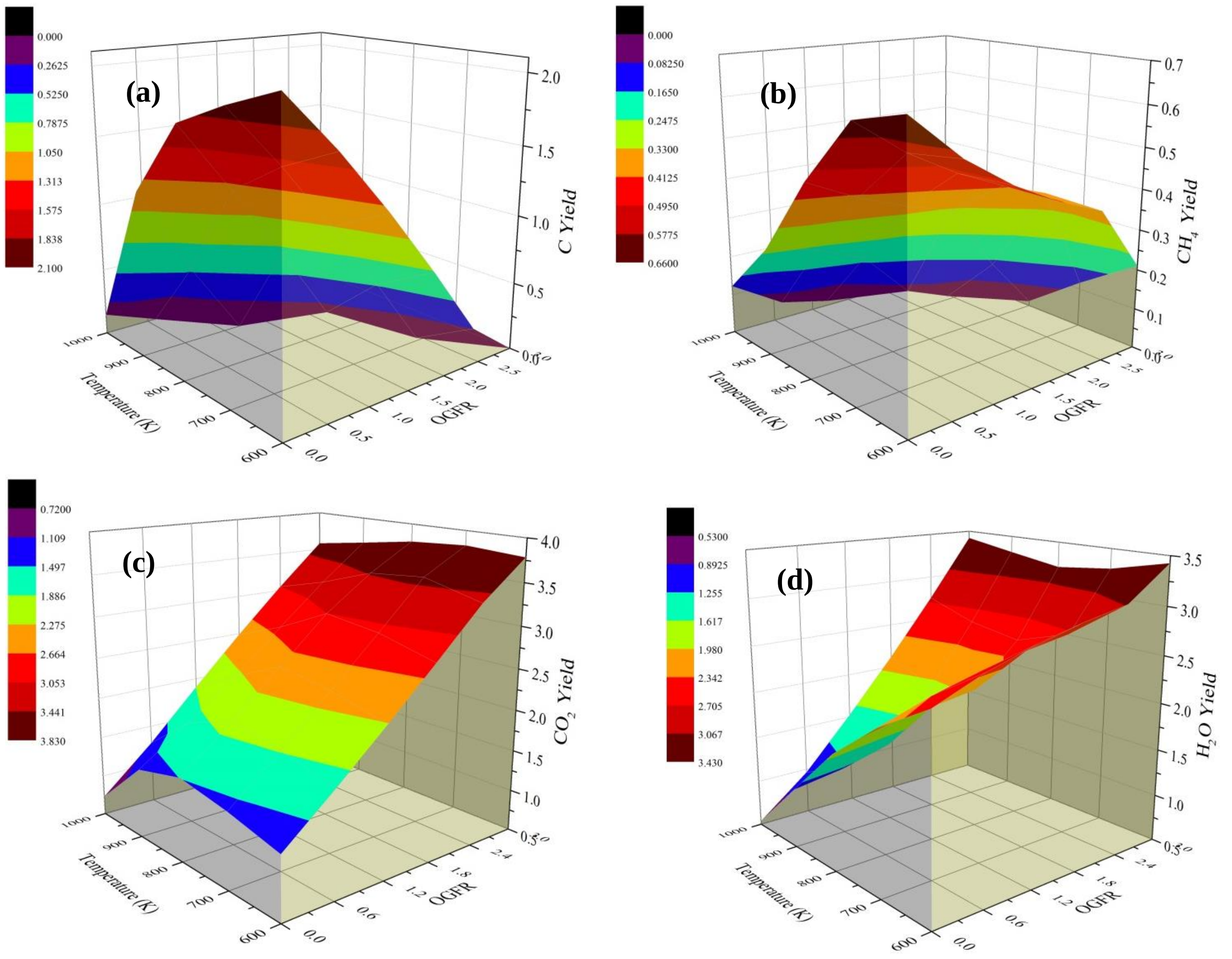

Figure B.10. Effect of temperature and OGFR on the yield of (a) solid carbon, (b) methane, (c) carbon dioxide and (d) water for the dry autothermal reforming of pure glycerol at atmospheric pressure and CGFR = 1.

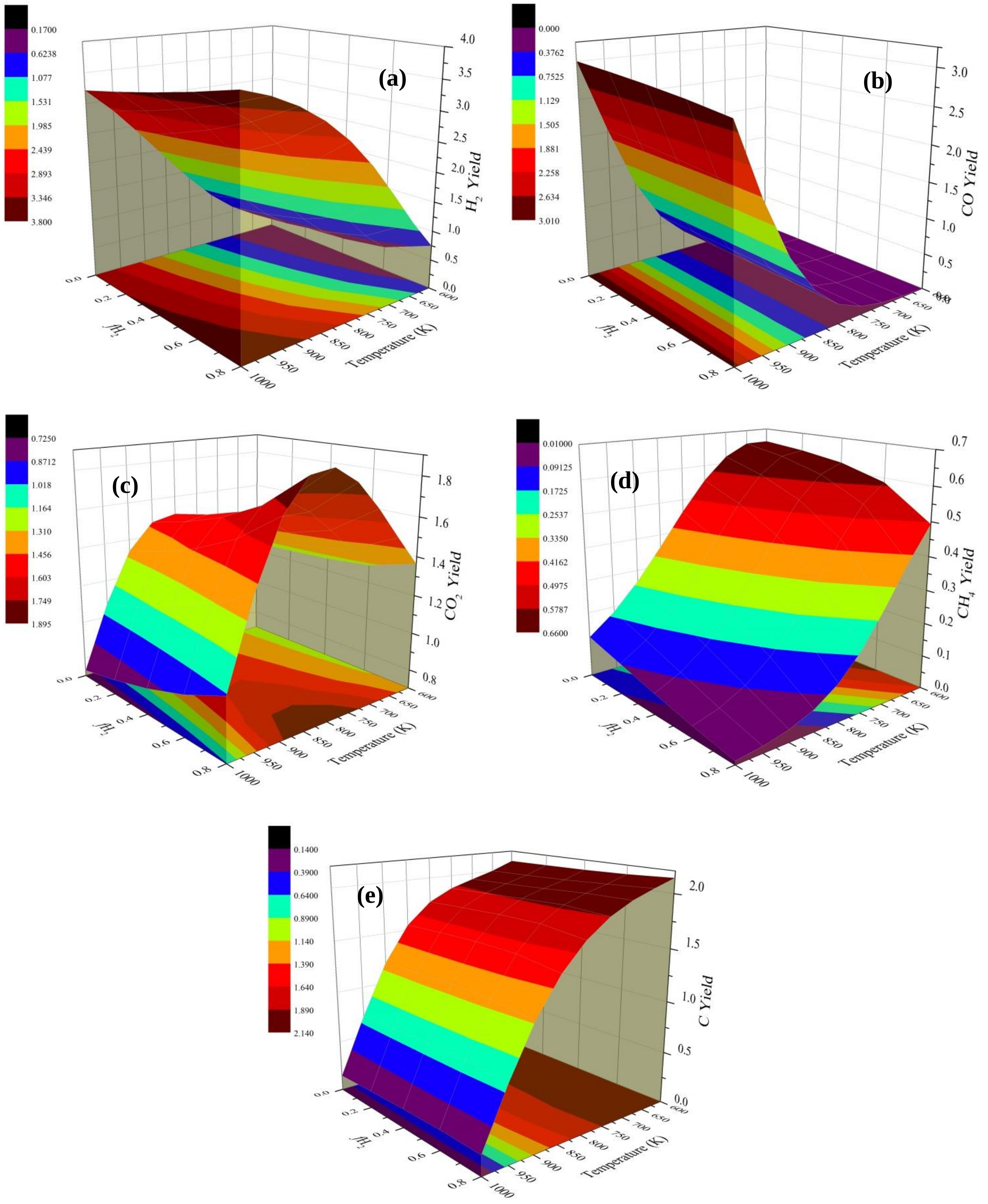

Figure B.11. Effect of temperature and removal fraction of H2 on the yield of (a) hydrogen, (b) carbon monoxide, (c) carbon dioxide, (d) methane and (e) solid carbon for the dry reforming of pure glycerol, at CGFR = 1 and 1 atm.