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RESEARCH ARTICLE

REVIEW ON THE TRI REFORMING PROCESS FOR SYNGAS PRODUCTION WITH BIOGAS IN WEST-AFRICA

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ABSTRACT

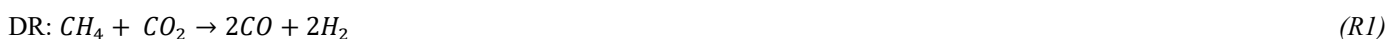
Biogas is produced by the anaerobic digestion of organic materials and could be utilized to produce syngas (H₂ and CO) via reforming technology such as tri reforming. Biogas tri reforming is a simultaneous combination of endothermic dry reforming and steam reforming with exothermic oxidation of methane, carried out in a single reactor to produce a syngas which is an important gas mixture feedstock to produce chemicals and energy carriers. Then, the process allows overcoming several weaknesses of each individual principal reforming process. This paper presents a literature review on recent achievements in biogas tri reforming process for syngas production in terms of processes description, parameters influencing, kinetics of reactions and Mathematical models and in the term of catalysts appropriate for the tri reforming. For this purpose, a swot analysis is carried out to identify the strengths, weaknesses and opportunities of each model in order to deduce gaps to be filled by the development of new approaches to modelling the tri reforming process.

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INTRODUCTION

The use of renewable energies sources, including biomass, is an asset to limit negative environmental impacts due to fossil fuels exploitation and use (1) . Biogas is a product derived from anaerobic digestion of biomass. It's composed by 50–75% (CH₄) , 25–45% (CO₂) , 2–7% (H₂O) and traces of other gases (1) . Biogas can be used for syngas production which is a mixture of CO, H₂ and a smaller percentage of CO₂. Syngas can be used as a raw material for synthetic fuels production with low environmental impact (hydrogen, ammoniac, aniline, methanol, ethanol, diesel, jet fuel, dimethyl ether synthetic gasolines, and other chemicals) (1) (2) (3) (4) . To produce syngas from biogas, there are three main reforming processes: Dry reforming (DR) (R1) , steam reforming (SRM) (R2) and partial oxidation (POM) (R3). The limits of each main reforming process have led to the development of other types of reforming. Thus, Song and Pan (5) proposed one process which is a combination of the three main processes on one reactor for production of syngas. This process is called Tri reforming (TRM).



Dry reforming is the reaction of carbon dioxide with methane that converting two major greenhouse gases with high global warming potential into valuable chemicals. Because the major constituents of the biogas are CH₄ and CO₂, dry reforming (DR) seems a suitable option. Dry reforming reaction (R1) is an endothermic reaction and necessitates temperature higher than 650°C. For Han *et al.* (6) , the range of operating temperature for DR is 700–950°C. Dry reforming yielded a lower syngas ratio (H₂/CO=1) , which is suitable for the synthesis of hydrocarbons from Fischer_Tropsch synthesis (7) and for the synthesis oxygenated chemicals (8) .

Syngas production from dry reforming of methane is influenced by the simultaneous occurrence of reverse water gas shift reaction (RWGS) (R4), which is result in a syngas ratio of unit (9). Although the dry reforming of methane has environmental benefits; it suffers from the problem of carbon deposition induced by methane decomposition (R5) and CO disproportionation or Boudouard reaction (R6). high temperatures requirement to reach high conversion levels, owing to the highly endothermic nature of the process and the carbon formation is the major drawback of DR. Catalyst deactivation by coke deposition (10) and/or sintering of the metallic phase and support of the catalyst (11) are/is resulted of the severe operating conditions of the process. The Steam Reforming (SRM) is a process in which methane is heated, with steam, to produce syngas in the presence of catalyst. It is an endothermic reaction, so it requires an external heat source as DR, this, reduces the overall efficiency of the fuel processor and of the global system (12). Compared with DR reaction, the steam reforming gives more hydrogen yields (13). The ratio of syngas produced in the steam reforming of methane is higher: $H_2/CO=3$ (4). This ratio is high compared that required for hydrogen production for example ($H_2/CO=1,5-2$) (7) (14). The process of steam reforming is energy intensive because of its high temperature ($900^\circ C$) to favor methane conversion and high steam to methane ratio ($S/C=3$) to limit the deactivation of the catalyst by coke deposition (15) (16) (17). Because of that, during syngas cooling to the temperature of downstream processes, energy is lost (18) (19). To produce higher yields of hydrogen, a higher H_2O/CH_4 ratio is required. This makes steam reforming of methane energetically unfavorable leading to the deactivation of the catalyst (38). Moreover, steam reforming faces corrosion issues and requires a desulphurization unit (20) (21). Steam reforming process requires high investments of capital (22). Partial oxidation of methane (POM) is a potential technology to increase the efficiency of syngas, compared to steam reforming. The main problem with the partial oxidation process is that, it can lead to hot spot generation, which can be dangerous and increases the possibility of explosions (23). Catalyst bed hot-spots; high cost of syngas purification to remove residual O_2 ; catalyst deactivation by re-oxidation of metallic nanoparticles, and coke deposition; fire hazard of O_2 and oxygen-enriched mixtures; etc., are the several drawbacks which can be involved in POM (24). The Tri reforming (TRM) proposed by Song is a combination of endothermic dry reforming and steam reforming with exothermic oxidation of methane, simultaneously carried out in a single reactor. The critical factors of single reactions: deactivation by coke during dry reforming and high endothermicity of dry and steam reforming through the presence of O_2 and H_2O in the reactive environment can be overcome by the simultaneous occurrence of the reactions. In this paper, the tri reforming process concept is reviewed at first time, then the mathematical models and the catalyst for tri reforming in a second time.

METHODOLOGY

To shed on biogas reforming, we searched for articles that discussed biogas reforming, then we selected those that dealt more with biogas tri reforming. A SWOT (Strengths, Weaknesses, Opportunities, Threats) analysis then allowed us to study each of its selected articles. Effort has been devoted to the development of biogas tri reforming as evidenced by the growing number of articles published, which has increased in recent years like showing in fig. 1. On the figure, the a) present the publications in Science Direct for research articles and review articles while the b) present only the publications in Google Scholar. The figures present the publications from 2012 to the half of 2022.

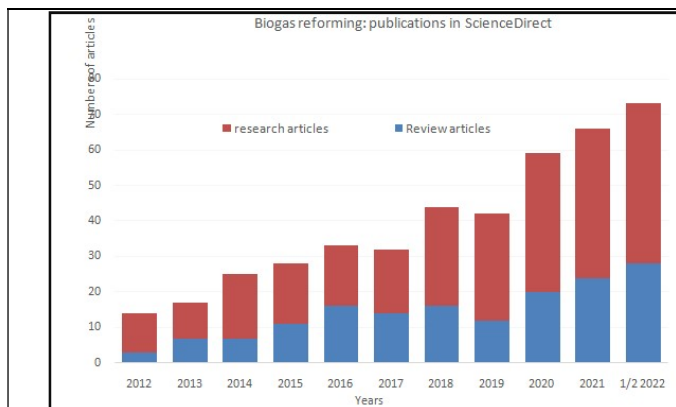


Fig.1: Search results on Web of science for “biogas reforming”, conducted on 02/07/2022: Publications in Science Direct

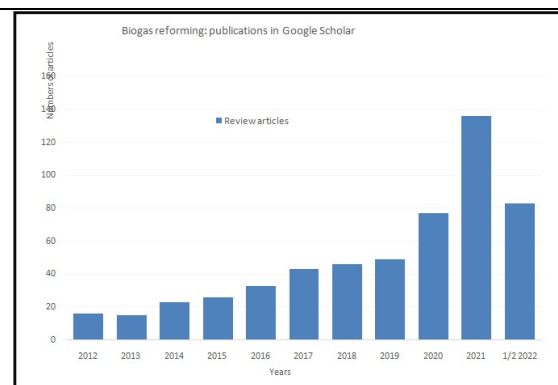


Fig.2: Search results on Web of science for “biogas reforming”, conducted on 02/07/2022: Publications in Google Scholar

PROCESSES DESCRIPTION: Pre heat biogas in a proper ratio (CO_2/CH_4 and H_2O/CH_4) and O_2 in a proper ratio with methane (O_2/CH_4) go through a single tri reformer reactor at a same time. Methane combustion occurs in the first time and supply heat for endothermic dry and steam reforming.

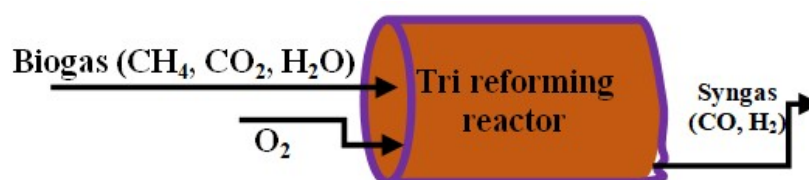


Fig. 3. Schematic diagram of tri reformer of biogas

This combination lead to a reduction in energy consumption. In the reaction system, O_2 and H_2O help to reduce the coke formation on the reforming catalyst and the H_2/CO ratio can be better controlled to the desired ratio. Table 1 shows the summary of advantages and disadvantages of tri reforming. Because of the significant advantages of tri-reforming, it has been studied extensively in recent years. S. Khajeh *et al.* (26) compared a fluidized-bed and fixed-bed and suggested a fluidized-bed reactor for a syngas production due to its special advantages such as elimination of pressure drop problem and bad temperature profile distribution. The enhancement in the methane conversion is 1.2% and 6% in CO_2 consumption in fluidized-bed tri-reformer reactor according to the comparison. the tri-reforming uses 45.8% and 19.7% less energy, compared with dry reforming of biogas and steam reforming of methane, respectively (27). Advantages and disadvantages of tri-reforming are summary in the Table 1.

Table 1. Advantages and disadvantages of tri-reforming (25) .

Advantages	Disadvantages
<ul style="list-style-type: none"> ➤ Directly using flue gases, rather than pre separated and purified CO₂ from flue gases ➤ High methane conversion can be achieved ➤ Eliminate CO₂ Separation ➤ Desired ratio of H₂/CO ➤ Minimize coke formation ➤ Make use of waste H₂O/O₂ ➤ Simplify processing system ➤ Useful tri-generation 	<ul style="list-style-type: none"> ➤ Usually requires oxygen plant ➤ No existing commercial catalysts ➤ Would require high GHSV ➤ Heat management ➤ Mass management ➤ Inert gas handling

Table 2: Reaction equilibrium constants and Arrhenius kinetic parameters (28) .

Reaction, j	Equilibrium constant, k_j	k_{oj} (mol/(kgcat s))	E_j (J/mol)
1	$K_I = \exp\left(\frac{-26830}{T_s} + 30.114\right)$ (bar ²)	$1.17 \times 10^{15} \text{bar}^{0.5}$	240,100
2	$K_{II} = K_I \cdot K_{III}$ (bar ²)	$2.83 \times 10^{14} \text{bar}^{0.5}$	243,900
3	$K_{III} = \exp\left(\frac{4400}{T_s} - 4.036\right)$	$5.43 \times 10^3 \text{bar}^{-1}$	67,130
4		$8.11 \times 10^5 \text{bar}^{-2}$ $6.82 \times 10^5 \text{bar}^{-2}$	86,000 86,000

$$k_j = k_{oj} \times \exp\left(\frac{-E_j}{RT}\right)$$

Table 3: Van't Hoff parameters for species adsorption (28) .

Components	k_{oi} (bar ⁻¹)	ΔH_i (J/mol)	K_{oi}^C (bar ⁻¹)	ΔH_i^C (J/mol)
CH ₄	6.65×10^{-4}	-38,280		
CO	8.23×10^{-5}	-70,650		
H ₂	6.12×10^{-9}	-82,900		
H ₂ O	$1.77 \times 10^5 \text{bar}$	88,680		
CH ₄ (combustion)			1.26×10^{-1}	-27,300
O ₂ (combustion)			7.78×10^{-7}	-92,800

$$K_i = K_{oi} \times \exp\left(-\frac{\Delta H_i}{RT}\right) \quad K_i^C = K_{oi}^C \times \exp\left(-\frac{\Delta H_i^C}{RT}\right)$$

Table 4. Physical properties, mass and heat transfer correlations (28) .

Parameter	Equation
Mass transfer coefficient between gas and solid phases.	$k_{gi} = 1.17 Re^{-0.45} Sc_i^{-0.67} u_g \times 10^3$ $Re = \frac{2R_p u_g \rho}{\mu}$ $Sc_i = \frac{\mu}{\rho D_{im} \times 10^{-4}}$ $D_{im} = \frac{1 - y_i}{\sum_{i \neq j} \frac{y_j}{D_{ij}}}$ $D_{ij} = \frac{10^{-7} T^{3/2} \sqrt{\frac{1}{M_i} + \frac{1}{M_j}}}{P (v_{ci}^{3/2} + v_{cj}^{3/2})^2}$
Overall heat transfer coefficient between steam reformer walls and the gas phase in the tube side	$\frac{1}{U_w} = \frac{1}{h_i} + \frac{A_i \ln\left(\frac{D_o}{D_i}\right)}{2\pi L K_w}$
Heat transfer coefficient between the gas phase and reactor wall	$\frac{h_i}{c_p \rho \mu} (c_p \mu)^{2/3} = \frac{0.458}{\epsilon_B} \left(\frac{\rho u d_p}{\mu}\right)^{-0.407}$

Table 5. Recent Studies on Tri-reforming of Biogas to Syngas

Catalyst	Reaction Conditions	CH ₄ Conv. (%)	CO ₂ Conv. (%)	H ₂ /CO	Coke Rate (gcoke/(gcat*h))	Ref.
Ni/MgO/CeZrO	850°, 32,000 mL/ (h*gcat) , 1 bar, CH ₄ /CO ₂ /O ₂ /H ₂ O = 1/0.21/0.1/0.81, fixed-bed reactor	~94	~55	~2.1	-	(5)
Ni/CeO ₂	800°C, CH ₄ /CO ₂ /O ₂ /H ₂ O = 1/0.67/0.1/0.3, 30,000 h ⁻¹ , 1 bar, continuous flow reactor	97.4–99.6	87.8–90.5	87.8–90.5	-	(1)
Ni/zeolite L	800°C, 162 h ⁻¹ , 1 bar, fixed-bed reactor	~86	~24	~1.9	-	(37)
Rh-Ni/zeolite L	800°C, 162 h ⁻¹ , 1 bar, fixed-bed reactor	96.4	~33	~1.8	-	(37)
Ni@SiO ₂	750°C, 1 bar, CH ₄ /CO ₂ /O ₂ /H ₂ O	73	43	1.7	0.028	(38)

	= 1/0.5/0.1/3.0, fixed-bed reactor					
Nickel-alumina aerogel	700°C, 269,000 mL/ (g*h) , 1 bar, fixed-bed reactor	83.3	-	2.0–2.1	3.5×10^{-3}	(39)
Ni/ZrO ₂	800°C, CH ₄ /CO ₂ /O ₂ /H ₂ O = 5/1/1/2.1, 80,000 mL/ (g*h) , 1 bar, fixed-bed reactor	84.4–98.5	89.3–98.5	1.6–2.2	-	(23)
Ni-Mg/CeO ₂ -ZrO ₂	800°C, 20,000 mL/ (g*h) , 1 bar, CH ₄ /CO ₂ /O ₂ /H ₂ O = 5/1/1/2.1, fixed-bed reactor	80.9–97.2	4.4–94.8	~2.1	-	(40)
NiMoC-Ce	850°C, CH ₄ /CO ₂ /O ₂ /H ₂ O = 1/0.39/0.16/0.30, fixed-bed reactor	~93	~100	-	-	(41)
NiMo-C	850°C, CH ₄ /CO ₂ /O ₂ /H ₂ O = 1/0.39/0.16/0.30, fixed-bed reactor	~96	~100	-	-	(41)
NiMoC-La	850°C, CH ₄ /CO ₂ /O ₂ /H ₂ O = 1/0.39/0.16/0.30, fixed-bed reactor	~93	~88	-	-	(41)
NiMoC-Mg	850°C, CH ₄ /CO ₂ /O ₂ /H ₂ O = 1/0.39/0.16/0.30, fixed-bed reactor	~90	~84	-	-	(41)
NiMoC-K	850°C, CH ₄ /CO ₂ /O ₂ /H ₂ O = 1/0.39/0.16/0.30, fixed-bed reactor	~17	~0	-	-	(41)
Ni/Ce-Zr-Al ₂ O ₃	800°C, 1 bar, 161 ggas* (gcat*h) 1, CH ₄ /CO ₂ /O ₂ /liquid H ₂ O = 1/0.67/0.25/0.0008, fixed-bed reactor	~99	~42	~1.9	-	(42)
Ni/Ce-Al ₂ O ₃	800°C, 1 bar, 161 ggas* (gcat*h) - 1, CH ₄ /CO ₂ /O ₂ /liquid H ₂ O = 1/0.67/0.25/0.0008, fixed-bed reactor	~99	~36	~1.9	-	(42)
Ni/Zr-Al ₂ O ₃	800°C, 1 bar, 161 ggas* (gcat*h) - 1, CH ₄ /CO ₂ /O ₂ /liquid H ₂ O = 1/0.67/0.25/0.0008, fixed-bed reactor	99	34	~2	-	(42)
Rh-Ni/Ce-Al ₂ O ₃	800°C, 1 bar, 161 ggas* (gcat*h) - 1, CH ₄ /CO ₂ /O ₂ /liquid H ₂ O = 1/0.67/0.25/0.0008, fixed-bed reactor	~99	~32	~2	-	(42)
Ni/Al ₂ O ₃	800°C, 1 bar, 17,220 mL* (g*h) -1, CH ₄ /CO ₂ /O ₂ /H ₂ O = 1/0.23/0.07/0.46, fixed-bed reactor	-	-	2.3	0.014	(43)
Ni/TiO ₂	800°C, 1 bar, 17,220 mL* (g*h) -1, CH ₄ /CO ₂ /O ₂ /H ₂ O = 1/0.23/0.07/0.46, fixed-bed reactor	-	-	1.9	2E-5	(43)
Ni/MgO	800°C, 1 bar, 17,220 mL* (g*h) -1, CH ₄ /CO ₂ /O ₂ /H ₂ O = 1/0.23/0.07/0.46, fixed-bed reactor	-	-	1.8	1.4E-3	(43)
Ni/SBA-15	800°C, 1 bar, 17,220 mL* (g*h) -1, CH ₄ /CO ₂ /O ₂ /H ₂ O = 1/0.23/0.07/0.46, fixed-bed reactor	-	-	2.2	1E-4	(43)
Ni/ZrO ₂	800°C, 1 bar, 17,220 mL* (g*h) -1, CH ₄ /CO ₂ /O ₂ /H ₂ O = 1/0.23/0.07/0.46, fixed-bed reactor	-	--	2.2	3.6E-3	(43)
Ni/CeO ₂ -ZrO ₂	800°C, 1 bar, 17,220 mL* (g*h) ⁻¹ , CH ₄ /CO ₂ /O ₂ /H ₂ O = 1/0.23/0.07/0.46, fixed-bed reactor	-	-	2.1	Negligible	(43)
NiO-Mg/Ce-ZrO ₂ /Al ₂ O ₃	827°C, CH ₄ /CO ₂ /O ₂ /H ₂ O = 1/1.33/0.47/2.47, 20 bar, multi-tubular reactor	~98	~12	~2.0	-	(44)
NiCe@SiO ₂	750°C, CH ₄ /CO ₂ /O ₂ /H ₂ O = 1/0.5/0.1/0.5, 1 bar, fixed-bed reactor, 60,000 mL/ (g*h)	79	75	1.7	-	(45)
Ni/TiO ₂ (calcined at 850 °C)	800 °C, CH ₄ /CO ₂ /O ₂ /H ₂ O = 1/0.23/0.07/0.46, 1 bar, tubular reactor, 17,220 mL/ (g*h)	-	-	2.0	Negligible	(46)

PARAMETERS INFLUENCING: A lot of parameters influence the TRM. Among this, we are the type of catalyst (including the support of catalyst), inlet feed temperature, composition of the reactant, the pressure. For Z. Arab Aboosadi *et al.* (28), there are independent parameters and dependent parameters that affect the performance of a tri reforming. Independent parameters are inlet feed temperature, CO₂/CH₄, H₂O/CH₄, O₂/CH₄, and pressure (28). Dependent parameters include reformer outlet temperature and conversion of methane. For Him, a key performance parameter is the molar ratio of H₂ produced in the reformer to methane feed. This molar ratio, multiplied by the ratio of low heating values (LHV) of H₂ to CH₄ results in the reformer fuel processor efficiency. The experimental show him that there is no significant effect on methane conversion at a fixed O₂/CH₄ ratio with inlet temperature in the range of 900–1100 K. This range of the inlet temperature is more suitable for the operation of reactor. The maximum yield of hydrogen is achieved for O₂/CH₄ in the range of 0.42–0.55 and same range of the temperature range. Higher H₂O/CH₄ generally yields more hydrogen, and the conversion of methane is higher. At a given H₂O/CH₄ ratio and at low oxygen level, the conversion is low since generated heat by combustion reaction is low. To maximize hydrogen yield and methane

conversion, there are optimum values of inlet feed temperature, CO₂/CH₄, steam/CH₄ and O₂/CH₄ ratios. Yishanet *et al.* (25), investigated the effect of temperature and pressure on equilibrium conditions during the tri reforming. The results reveal that high temperature (800°C – 900°C) and low pressure favor the high H₂ production and CO₂ conversion. The study of the combined effect of the parameters (temperature, O₂/CH₄, CO₂/CH₄, H₂O/CH₄) two-by-two on the equilibrium conditions was also carried out. Combined effect of the O₂/CH₄ and temperature on equilibrium conditions show that low temperature and high O₂ content are not favorable in tri reforming. For the combined effect of the H₂O/CH₄ and temperature on equilibrium conditions, it was observed that 100% CH₄ conversion was achieved, regardless of the H₂O content (25). A significant decrease of CO₂ conversion is caused by increasing of the H₂O content, but this increasing does not contribute to any increase of H₂O conversion at high temperature. About the H₂/CO ratio, it tends to increase with increasing of H₂O content, showing that H₂O accretion enhance H₂ yield and dampens the RWGS. Combined effect of the CO₂/CH₄ and temperature on equilibrium conditions revealed that H₂ and CO yields reduce considerably with the addition of CO₂ above 700°C but the increasing of CO₂/CH₄ ratio and temperature led the increasing of CH₄ conversion. According to a combined effect of the O₂/CH₄ and H₂O/CH₄ on equilibrium conditions, an increase in the H₂O/CH₄ ratio decreases the H₂ yield at a given O₂/CH₄ ratio and the increase of O₂ and H₂O contents leads to a decrease of CO₂ conversion.

O₂/CH₄ ratio higher than 0.2 or a H₂O/CH₄ ratio higher than 0.5 is located as the carbon-free region. An increasing of O₂ and CO₂ contents led to a decrease of H₂ yield was observed in the study of combined effect of the O₂/CH₄ and C₂O/CH₄ on equilibrium conditions. According to this study, very low values of both O₂/CH₄ and CO₂/CH₄ ratios are defined as the carbon formation domain. The last combined effect investigate is the combine effect of H₂O/CH₄ and CO₂/CH₄ on equilibrium conditions. It was observed that H₂ yield decreases with the increase of H₂O/CH₄ and CO₂/CH₄ ratios but where the CO₂/CH₄ ratio is higher than 0.8 or the H₂O/CH₄ ratio is higher than 0.6, no carbon formation takes place. CH₄/CO₂/H₂O/O₂ = 1:0.291:0.576:0.088 is identified as the optimum feed ratio in tri-reforming process to attain the maximum H₂ yield, and high CO₂ conversion coupled with a desired synthesis gas (H₂/CO) ratio for the downstream methanol production and effective elimination of carbon formation. The thermodynamic analysis of the biogas tri-reforming process at different temperatures (850–1000°C) and feed compositions was investigated by Diez-Ramirez *et al.* (29). CH₄/CO₂/H₂O/O₂ = 4:1:4:2 is defined as the optimal molar feed composition where more than 90% of methane conversion, high H₂/CO ratio (H₂/CO = 2), higher thermal efficiency (>70%), were achieved. Moreover, 98.04% of methane conversion was achieved with the reaction temperature of 950°C and desired H₂/CO ratio (H₂/CO = 2.01). The destruction of exergy mainly unfortunately occurred in the reactor, mostly due to the high irreversibility of the chemical reactions. Future research should focus on reducing the exergy destruction within the reactor and heat exchanger (29). Zhao *et al.* (30) investigated the thermodynamic equilibrium analysis of tri-reforming using surrogate biogas at conditions of pressure (3 bar), temperatures (830°C and 860°C), and H₂O to CH₄ molar ratios (0.34, 0.69, 1.40, and 2.10). At all conditions, the equilibrium O₂ conversions were nearly 100%. The equilibrium CH₄ conversion increased from 95% to 99%, and with the increase of the H₂O to CH₄ molar ratio, the equilibrium CO₂ conversion decreased from 71% to 8%. What's more, H₂/CO molar ratio increased with the H₂O/CH₄ molar ratio increased. In addition, the equilibrium CH₄ conversion increases with the increase of the H₂O/CH₄ molar ratio. However, since O₂ and H₂O are more reactive with CH₄, the presence of O₂ and H₂O decrease the CO₂ conversion. An investigation on the parametric study on catalytic tri-reforming of methane for syngas production conducted by Rei-Yu *et al.* (31), showed that high temperature is resulted with higher O₂ content in reactant, leading to lower H₂/CO ratio high temperature is resulted with higher O₂ content in reactant, leading to lower H₂/CO ratio. The absence of H₂O and of CO₂ in the reactant results respectively in the dry reforming becoming the dominant reaction in the tri reforming, leading to H₂/CO ratio close to unity, and in the steam reforming becoming the dominant reaction in the tri reforming, leading to a H₂/CO ratio close to 3. Due to the catalyst kinetic limitation, the tri reforming cannot be activated if the reactant inlet temperature is too low (T<400°C) (31). Then, high temperature flue gas was suggested for the activation. The temperature and species mole fraction distributions are not affected by the delay factor at the reactor outlet. An insignificant effect on the temperature distribution is produced by the H₂O amount effect. Then H₂O addition does not affect the catalytic behavior of the catalyst bed. The WGS reaction plays an important role in H₂ and CO yields. Because the reactor temperature is not affected by the CO₂/CH₄ ratio significantly, CH₄ conversion is not affected by the CO₂/CH₄ ratio to a large extent. Xianhui Zhao *et al.* (2) have reviewed the biogas reforming to syngas in general. The investigation revealed that several factors affect biogas reforming including temperature, pressure, feed gas composition, space velocity, and catalyst activity. High reaction temperature (>800°C) is requested to obtain high CH₄ and CO₂ conversions due to the endothermic nature, but high pressure can suppress reactions to decrease CH₄ and CO₂ conversions (2). The tri-reforming of biogas seems to be an advanced technology toward high conversions of reactants, compared with other reforming methods (e.g., dry and bi-reforming). But, during the tri-reforming process, the CO₂ conversion needs to be improved.

KINETICS OF REACTIONS AND MATHEMATICAL MODELS: Despite tri forming is characterize by three main reactions, four global reactions are generally used to describe the process (R7) - (R10) (32). In these reactions, the reaction of dry reforming (R1) is use as reaction (R7) minus reaction of water gas shift (R9) since the kinetic rate expression have been validated in the literature.



Wonjun Cho *et al.* (32) developed a first principle model for the tri-reforming reactor. Homogeneous gas-phase reactions and heterogeneous catalytic reactions are combining for a kinetic mechanism. To describe the heterogeneous part, effective rate equations proposed by Smet *et al.* (33) are used.

$$\text{For (R10)} : r_1 = \frac{K_{1a}P_{\text{CH}_4}P_{\text{O}_2}}{(1+K_{\text{CH}_4}^{\text{OX}}P_{\text{CH}_4}+K_{\text{O}_2}^{\text{OX}}P_{\text{O}_2})^2} + \frac{K_{1b}P_{\text{CH}_4}P_{\text{O}_2}}{(1+K_{\text{CH}_4}^{\text{OX}}P_{\text{CH}_4}+K_{\text{O}_2}^{\text{OX}}P_{\text{O}_2})} \quad (1)$$

$$\text{For (R7)} : r_2 = \frac{K_2^{\text{XU}}/P_{\text{H}_2}^{2,5}(P_{\text{CH}_4}P_{\text{H}_2\text{O}}-P_{\text{H}_2}^3P_{\text{CO}}/K_{\text{eq},2})}{(1+K_{\text{CO}}P_{\text{CO}}+K_{\text{H}_2}P_{\text{H}_2}+K_{\text{CH}_4}P_{\text{CH}_4}+K_{\text{H}_2\text{O}}P_{\text{H}_2\text{O}}/P_{\text{H}_2})^2} \quad (2)$$

$$\text{For (R9)} : r_3 = \frac{K_2^{\text{XU}}/P_{\text{H}_2}(P_{\text{CO}}P_{\text{H}_2\text{O}}-P_{\text{H}_2}P_{\text{CO}_2}/K_{\text{eq},3})}{(1+K_{\text{CO}}P_{\text{CO}}+K_{\text{H}_2}P_{\text{H}_2}+K_{\text{CH}_4}P_{\text{CH}_4}+K_{\text{H}_2\text{O}}P_{\text{H}_2\text{O}}/P_{\text{H}_2})^2} \quad (3)$$

$$\text{For (R8)} : r_4 = \frac{K_2^{X_u} / P_{H_2}^{3.5} (P_{CH_4} P_{H_2O}^2 - P_{H_2} P_{CO_2} / K_{eq,4})}{(1 + K_{CO} P_{CO} + K_{H_2} P_{H_2} + K_{CH_4} P_{CH_4} + K_{H_2O} P_{H_2O} / P_{H_2})^2} \quad (4)$$

The validated model is used for the optimization of design variables and operational variables such as the feed composition. He got with the model, 90% of the methane conversion, and unit for the ratio of hydrogen and carbon. This ratio is not interesting because too low. Z. Arab Aboosadi *et al.* (25) used the model of Xu and Froment (34) for reaction (R7) – (R9) and the model of Trimm and Lam (35) for reaction (R10) to determine the rate of consumption or formation of specie as:

$$r_{CH_4} = -\eta_1 R_1 - \eta_2 R_2 - \eta_4 R_4 \quad (5)$$

$$r_{O_2} = -2\eta_4 R_4 \quad (6)$$

$$r_{CO_2} = \eta_2 R_2 + \eta_3 R_3 + \eta_4 R_4 \quad (7)$$

$$r_{H_2O} = -\eta_1 R_1 - 2\eta_2 R_2 - \eta_3 R_3 + 2\eta_4 R_4 \quad (8)$$

$$r_{H_2} = 3\eta_1 R_1 + 4\eta_2 R_2 + \eta_3 R_3 \quad (9)$$

$$r_{CO} = \eta_1 R_1 - \eta_3 R_3 \quad (10)$$

Where $\eta_1 = 0.07, \eta_2 = 0.06, \eta_3 = 0.7, \eta_4 = 0.05$ (36) and

$$R_1 = \frac{k_1}{P_{H_2}^{2.5}} \left(P_{CH_4} P_{H_2O} - \frac{P_{H_2}^3 P_{CO}}{K_I} \right) \times \frac{1}{\phi^2} \quad (11)$$

$$R_2 = \frac{k_2}{P_{H_2}^{3.5}} \left(P_{CH_4} P_{H_2O}^2 - \frac{P_{H_2}^4 P_{CO_2}}{K_{II}} \right) \times \frac{1}{\phi^2} \quad (12)$$

$$R_3 = \frac{k_3}{P_{H_2}} \left(P_{CO} P_{H_2O} - \frac{P_{H_2} P_{CO_2}}{K_{III}} \right) \times \frac{1}{\phi^2} \quad (13)$$

$$R_4 = \frac{k_{4a} P_{CH_4} P_{O_2}}{(1 + K_{CH_4}^C P_{CH_4} + K_{O_2}^C P_{O_2})^2} + \frac{k_{4b} P_{CH_4} P_{O_2}}{(1 + K_{CH_4}^C P_{CH_4} + K_{O_2}^C P_{O_2})} \quad (14)$$

$$\phi = 1 + K_{CO} P_{CO} + K_{H_2} P_{H_2} + K_{CH_4} P_{CH_4} + K_{H_2O} \frac{K_{H_2O}}{P_{H_2}} \quad (15)$$

The reaction equilibrium constants and Arrhenius kinetic parameters, and the Van't Hoff parameters for species adsorption are showing in the table 2 and 3 respectively. To determine the concentration and temperature distributions inside the reactor, a one-dimensional heterogeneous model has been developed. Considering a differential element along the axial direction inside the react, the mass and energy balance equations are expressed by:

•for the solid phase

$$k_{gi}(y_i - y_{is}) + \eta r_i \rho_B \alpha = 0 \quad (16)$$

$$a_v h_f (T - T_s) + \rho_B \alpha \sum_{i=1}^N \eta r_i (-\Delta H_{fi}) = 0 \quad (17)$$

The reaction equilibrium constants and Arrhenius kinetic parameters are showing in the table 4.

•for the fluid phase

$$-\frac{F_t}{A_a} \frac{\partial y_i}{\partial z} + a_v c_t k_{gi}(y_{is} - y_i) = 0 \quad (18)$$

$$-\frac{1}{A_a} c_{pg} \frac{\partial (F_t T)}{\partial z} + a_v h_f (T_s - T) + \frac{\pi D_i}{A_a} U_w (T_w T) = 0 \quad (19)$$

with the model, he obtained 97,9% of the methane conversion, and 1,7 for the ratio of hydrogen and carbon. This ratio is good for the syngas. Yishan Zhang *et al.* (25) are used total Gibbs energy minimization to understand the effects of process variables on the product distribution. The expression of the total Gibbs free energy of the system over N species is:

$$G^t = \sum_{i=1}^N n_i G_i^0 + R(T + 273.15) \sum_{i=1}^N n_i \ln \frac{f_i}{f_i^0} + n_s G_s \quad (20)$$

With:

n_i : number of moles of species i

G_i^0 : Gibbs free energy of species i under standard conditions,

R: universal molar gas constant,

T: temperature in degrees Celsius

f_i^0 and f_i are: fugacity of species i at standard and operating conditions respectively,

ns: number of solid carbon molecules formed,

Gs: Gibbs free energy of solid carbon at the operating conditions.

To determine the performance of tri-reforming reactions, he defined the equilibrium CO₂, CH₄, and H₂O conversions and H₂ and CO yields as:

Conversion of CO₂

$$\text{CO}_2(\%) = \frac{(F_{\text{CO}_2,\text{in}} - F_{\text{CO}_2,\text{out}})}{F_{\text{CO}_2,\text{in}}} \times 100\% \quad (21)$$

Conversion of CH₄

$$\text{CH}_4(\%) = \frac{(F_{\text{CH}_4,\text{in}} - F_{\text{CH}_4,\text{out}})}{F_{\text{CH}_4,\text{in}}} \times 100\% \quad (22)$$

Conversion of H₂O

$$\text{H}_2\text{O}(\%) = \frac{(F_{\text{H}_2\text{O},\text{in}} - F_{\text{H}_2\text{O},\text{out}})}{F_{\text{H}_2\text{O},\text{in}}} \times 100\% \quad (23)$$

$$\text{H}_2 \text{ yield}(\%) = \frac{F_{\text{H}_2,\text{out}}}{2F_{\text{CH}_4,\text{in}} + F_{\text{H}_2\text{O}}} \times 100\% \quad (24)$$

$$\text{CO yield}(\%) = \frac{F_{\text{CO},\text{out}}}{F_{\text{CH}_4,\text{in}} + F_{\text{CO}_2,\text{in}}} \times 100\% \quad (25)$$

where F represents the flow rate of each gas species denoted by its respective subscript. The analyses reveal that high temperature and low pressure are favorable to achieve high H₂ production and CO₂ conversion. CH₄/CO₂/H₂O/O₂ = 1:0.291:0.576:0.088 is defined as the optimum to attain the maximum H₂ yield, high CO₂ conversion and desired synthesis gas (H₂/CO) ratio for the downstream methanol production and effective elimination of carbon formation. Rei-Yu Chein *et al.* (31) introduced N₂ into a reactor from the reactor bottom as the balanced inert gas in the reaction and characterize the performance of the system as:

Conversion of CH₄:

$$X_{\text{CH}_4} = \frac{F_{\text{CH}_4,\text{in}} - F_{\text{CH}_4,\text{out}}}{F_{\text{CH}_4,\text{in}}} \times 100\% \quad (26)$$

$$\text{H}_2 \text{ yield: } Y_{\text{H}_2} = \frac{F_{\text{H}_2,\text{out}} - F_{\text{H}_2,\text{in}}}{F_{\text{CH}_4,\text{in}}} \quad (27)$$

$$\text{CO yield: } Y_{\text{CO}} = \frac{F_{\text{CO},\text{out}} - F_{\text{CO},\text{in}}}{F_{\text{CH}_4,\text{in}}} \quad (28)$$

$$\text{H}_2/\text{CO ratio: } \text{H}_2/\text{CO} = \frac{F_{\text{H}_2,\text{out}}}{F_{\text{CO},\text{out}}} \quad (29)$$

With: i in F, and i out F, : molar flow rates at the reactor inlet and outlet of the i th species respectively. The model was validated using the experimentally verified numerical results reported by Arab Aboosadi *et al.* Equations for the mass conservation, fluid flow, energy transport and species transport are used to describe transport phenomena in the tubular fixed-bed reactor as (26) :

•Fluid flow

$$\nabla \cdot (\varepsilon \rho \vec{V}) = 0 \quad (30)$$

$$\frac{1}{\varepsilon^2} \nabla \cdot (\rho \vec{V} \vec{V}) = \nabla \cdot \left[-p \vec{1} + \frac{\mu_m}{\varepsilon} (\nabla \vec{V} + (\nabla \vec{V})^T) - \frac{2\mu_m}{3} \vec{1} \nabla \cdot \vec{V} \right] - \frac{\mu_m}{K} \vec{V} - \frac{\rho C_F}{\sqrt{K}} |\vec{V}| \vec{V} \quad (31)$$

•Energy transport

$$\nabla \cdot (\varepsilon \rho C_p \vec{V} T) = \nabla \cdot (\lambda_c \nabla T) + q_c \quad (32)$$

•Maxwell-Steffan species transport

$$\nabla \cdot \left\{ \varepsilon \rho \vec{V} m_i - \rho m_i \sum_{j=1}^{N_G} [D_{ij} (\nabla x_j + (x_j - m_j) \frac{\nabla p}{p}) - D_i^T \frac{\nabla T}{T}] \right\} = R_i \quad (33)$$

Based on the model of Xu Froment (34) Eqs. (11) - (13) and the model of Trimm and Lam (35) Eq. (14) , the energy source term q_c and species production/destruction rate R_i appeared in Eqs. (32) and (33) can be written as:

$$q_c = \sum_{i=1}^4 \eta_i r_i [\Delta H_{298K,i}^0 + \Delta H_{T-298K,i}] \quad (34)$$

$$R_{\text{CH}_4} = \rho_{\text{cat}}(-\eta_1 r_1 - \eta_3 r_3 - \eta_4 r_4) \quad (35)$$

$$R_{\text{O}_2} = \rho_{\text{cat}}(-2\eta_4 r_4) \quad (36)$$

$$R_{\text{H}_2\text{O}} = \rho_{\text{cat}}(-\eta_1 r_1 - \eta_2 r_2 - 2\eta_3 r_3 + 2\eta_4 r_4) \quad (37)$$

$$R_{\text{CO}_2} = \rho_{\text{cat}}(\eta_2 r_2 + \eta_3 r_3 + \eta_4 r_4) \quad (38)$$

$$R_{\text{CO}} = \rho_{\text{cat}}(-\eta_1 r_1 - \eta_2 r_2) \quad (39)$$

$$R_{\text{H}_2} = \rho_{\text{cat}}(3\eta_1 r_1 + \eta_2 r_2 + 4\eta_3 r_3) \quad (40)$$

In Eq. (34) $\Delta H_{298\text{K},i}^0$ is the standard heat of reaction of the i th reaction, $\Delta H_{T-298\text{K},i}$ is the correction for heat of reaction due to temperature change and can be written as (31),

$$\Delta H_{T-298\text{K},i} = \left(\sum_{\text{product}} v_{ij} \bar{c}_{p,ij} - \sum_{\text{reactant}} v_{ij} \bar{c}_{p,ij} \right) (T - 298) \quad (41)$$

In Eqs. (35) - (40), ρ_{cat} is the catalyst density which is the ratio of catalyst weight to fixed-bed volume. In Eq. (41), v_{ij} and $\bar{c}_{p,ij}$ are the stoichiometric coefficient and molar specific heat of species j in reaction i , respectively. The effect of kinetic model proposed by Numaguchi and Kikuchi of steam methane reforming reaction on TRM performance was also study by Rei-Yu Chein *et al.* (2016). The model is based on nickel and is defined as:

$$\text{SRM: } t_1 = \frac{k_1^{\text{NK}} \left(P_{\text{CH}_4} \frac{P_{\text{H}_2}^3 P_{\text{CO}}}{K_{\text{eq},1}} \right)}{P_{\text{H}_2\text{O}}^{0.596}} \quad (42)$$

$$\text{WGS: } t_2 = k_2^{\text{NK}} \left(P_{\text{CO}} P_{\text{H}_2\text{O}} - \frac{P_{\text{H}_2} P_{\text{CO}_2}}{K_{\text{eq},2}} \right) \quad (43)$$

$$\text{RCM: } t_2 = 0 \quad (44)$$

k_1^{NK} is the rate constant. The limit of this model is that the reverse CO₂ methanation reaction was not included in the kinetic model proposed by Numaguchi and Kikuchi (34).

CATALYSTS

The tri reforming is a catalytic reaction, then the process needs a solid catalyst to achieve significant rates and yields at reasonable temperatures. However, the development of an active, selective, and stable catalyst remains a major challenge for this process since the catalysts used for steam and dry reforming are not suitable for the tri reforming. The main criterion in the catalyst selection for the tri reforming is its ability to catalyze the three reforming reactions that characterize it. Ni catalysts supported on a wide range of different support materials with low concentration of Lewis sites, and/or support materials that can develop strong interaction metal-support coupled with high oxygen storage properties are the most popular use in tri reforming. Among this support materials, we are Al₂O₃, ZrO₂, MgO, La₂O₃, TiO₂, CeO₂, TiO₂, CeZrO, SiO₂...

Song and Pan (19) found that, in the tri-reforming in the temperature range of 700–850°C, the type and nature of catalysts have a significant impact on CO₂ conversion in the presence of H₂O and O₂. Among the catalysts they tested for tri-reforming, their ability to enhance the conversion of CO₂ follows the order of Ni/MgO > Ni/MgO/CeZrO > Ni/CeO₂ ≈ Ni/ZrO₂ ≈ Ni/Al₂O₃ > Ni/CeZrO (5). Xuan-Huynh Pham *et al.* (19) have listed the criteria required for an efficient catalyst support. Among this, there are: high thermal stability, high specific surface area for active phase dispersion, high basicity for adsorption of CO₂ and coke limitation, adequate MSI for metal reduction capacity and thermal sintering resistance, frequently presence of oxygen vacancies and high oxygen storage capacity for coke elimination, and affordable cost (19). The use of promoters can improve catalyst performance. In tri reforming, with have like promoters, s-block elements (alkali and alkaline earth metals) and d- and f-block elements. Mixed oxides doped with MgO, CeO₂, ZrO₂, and La₂O₃ are strongly suggested for future works by Xuan-Huynh Pham *et al.* (19). Table 5 summarizes the different catalysts with various supports and different biogas compositions that have been investigated and developed to improve the catalytic performance for the biogas tri-reforming.

CONCLUSION

Tri reforming have gained greater attention in recent years. In this work, the tri-reforming process for syngas production with biogas has been reviewed in terms of processes description, parameters influencing, kinetics of reactions and Mathematical models and in the term of catalysts appropriate for the tri reforming. In summary, tri-reforming of biogas has the potential advantages of combining all the three reforming processes in a single reformer unit to produce syngas. This process uses 45.8% and 19.7% less energy, compared with dry reforming of biogas and steam reforming of methane, respectively. But it is affected by several factors including the type of catalyst (including the support of catalyst), inlet feed temperature, composition of the reactant, the pressure. High temperature (800°C – 900°C) and low pressure favor the high H₂ production and CO₂ conversion. But the optimal feed gas composition (CH₄/CO₂/H₂O/O₂) and the best catalyst remain a challenge for the process even if the catalyst based on the nickel is the best. The kinetics of reactions and Mathematical models must be improved. Finally, the economic evaluation of the tri reforming of biogas could be investigated.

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Nomenclature

A	cross section area of reactor, m ²
av	specific surface area of catalyst pellet, m ² /m ³
Ar	Archimedes number
ab	specific surface area of bubble, m ² /m ³
Cp	specific heat of the gas at constant pressure, J/kg.K
Ct	total concentration, mol/m ³
Di	inner diameter, m
Do	outside diameter of steam reformer, m
dp	particle diameter, m
db	bubble diameter, m
Ft	total molar flow, mol/s
Fb	molar flow in bubble side, mol/s
Fe	molar flow in emulsion side, mol/s
hf _{gas–solid}	heat transfer coefficient, W/m ² .K
hi	heat transfer coefficient between fluid phase and reactor wall, W/m ² .K
k1	reaction rate constant for the first rate equation, mol/kg.s
k2	reaction rate constant for the second rate equation, mol/kg.s
k3	reaction rate constant for the third rate equation, mol/kg.s
k4a	first reaction rate constant for the fourth rate equation, mol/kg.s
k4b	second reaction rate constant for the fourth rate equation, mol/kg.s
Kbei	mass transfer coefficient for component i in fluidized-bed, m/s
Kw	thermal conductivity of reactor wall, W/m.K
Mi	molecular weight of component i, g/mol
N	number of components
Pi	partial pressure of component i in reaction side, bar
ri	reaction rate of component i, mol/kg.s
rbi	reaction rate of component i in bubble phase, mol/kg.s
rei	reaction rate of component i in emulsion phase, mol/kg.s
R1	first rate of reaction for steam reforming of CH ₄ (R7), mol/kg.s
R2	second rate of reaction for steam reforming of CH ₄ (R8), mol/kg.s
R3	water gas shift reaction (R9), mol/kg.s
R4	rate for total combustion of CH ₄ (R10), mol/kg.s
R	universal gas constant, J/mol.K
Re	Reynolds number
Sci	Schmidt number of component
T	bulk gas phase temperature, K

T_s	temperature of solid phase, K
T_w	wall temperature of steam reformer, K
U	superficial velocity of fluid phase, m/s
u_b	velocity of rise of bubbles, m/s
u_g	linear velocity of fluid phase, m/s
U_w	overall heat transfer coefficient between tube wall and reaction side streams in steam reformer, W/m ² .K
v_{ci}	critical volume of component i, cm ³ /mol
y_{ib}	mole fraction of component i in the bubble phase, mol/mol
y_{ie}	mole fraction of component i in the emulsion phase, mol/mol
y_i	mole fraction of component i in the fluid phase, mol/mol
y_{is}	mole fraction of component i in the solid phase, mol/mol
Z	axial reactor coordinate, m

Greek letters

α	activity of catalyst (where $\alpha = 1$ for fresh catalyst)
ϵ	Catalyst bed porosity
ρ	density, kg/m ³
ρ_B	density of catalytic bed, kg/m ³
ρ_e	density of emulsion phase, kg/m ³
ρ_g	density of fluid phase, kg/m ³
ρ_p	density of catalyst, kg/m ³
ΔH_{fi}	enthalpy of formation of component i, J/mol
ΔH_{298}	enthalpy of reaction at 298 K, J/mol
η	catalyst effectiveness factor
λ	thermal conductivity, W/m.K
μ	viscosity of fluid phase, kg/m.s

Subscript

in	inlet
m	gas mixture
out	outlet
R	reaction
ref	reference state
cat	catalyst
I	component i
J	reaction number index
P	particle
