



Simulation of methanol production from residual biomasses in a Cu/ZnO/Al₂O₃ packed bed reactor

Simulación de la producción de metanol usando biomazas residuales en un reactor empacado de Cu/ZnO/Al₂O₃

Carlos Esteban Aristizábal Alzate ^{1*}, Pedro Nel Alvarado Torres ¹, Andrés Felipe Vargas Ramírez ¹

¹Grupo de Investigación en Materiales Avanzados y Energía, MATYER, Facultad de Ingeniería. Instituto Tecnológico Metropolitano de Medellín (ITM). Calle 73 No. 76A – 354, Vía al Volador. C. P. 050036. Medellín, Colombia.

CITE THIS ARTICLE AS:

C. E. Aristizábal, A. F. Vargas and P. N. Alvarado.

"Simulation of methanol production from residual biomasses in a Cu/ZnO/Al₂O₃ packed bed reactor", *Revista Facultad de Ingeniería Universidad de Antioquia*, no. 102, pp. 115-124, Jan-Mar 2022. [Online]. Available: <https://www.doi.org/10.17533/udea.redin.20200907>

ARTICLE INFO:

Received: November 28, 2019
Accepted: September 23, 2020
Available online: September 23, 2020

KEYWORDS:

Methanol; SYNGAS; catalyst; simulation

Metanol; SYNGAS; catalizador; simulación

ABSTRACT: This article aims to simulate an algorithm constructed in MATLAB to represent the catalytic conversion of SYNGAS into methanol in a packed-bed reactor, based on chemical kinetics for a heterogeneous system with a Cu/ZnO/Al₂O₃ as a catalyst, and complementary math and phenomenological models, as a pressure drop and catalyst deactivation. Model validation is developed, comparing reference results and the results by running the algorithm in MATLAB using a reference SYNGAS composition. Also, the constructed model considers a catalyst deactivation by sintering and pressure drop along the reactor. Several parameters were evaluated to identify the pro conditions for methyl alcohol production; these parameters include the gasifying agent selection, the biomass and steam ratio effect, and the biomass origin.

RESUMEN: El objetivo de este artículo es simular un algoritmo construido en MATLAB para representar la conversión catalítica de SYNGAS en metanol en un reactor de lecho empacado, basados en la cinética química para un sistema heterogéneo con un Cu/ZnO/Al₂O₃ como catalizador, y en modelos matemáticos y fenomenológicos, como caída de presión y desactivación del catalizador. Se realiza una validación del modelo, comparando los resultados de referencia y los resultados obtenidos al ejecutar en el algoritmo MATLAB la composición de referencia SYNGAS. Además, el modelo construido considera una desactivación del catalizador por sinterización y caída de presión a lo largo del reactor. Se evaluaron varios parámetros para identificar las condiciones para la producción de alcohol metílico; Estos parámetros incluyen la selección del agente gasificante, el efecto de la relación de biomasa y vapor y el origen de la biomasa.

1. Introduction

Methanol is an important fuel and promising energy vector, since it has an octane number of 113 and its energy density is near half of the gasoline (by volume); blends of 10%/90% methanol/gasoline can lead to an octane level up to 130 and pure methanol engines can reach efficiency close to 43% [1]. Besides, it is an essential input for biodiesel production, participating with about 10% to 15% of the total

raw materials used in the production of this biofuel [2, 3], and is a precursor for many other high-value chemical compounds, generally and industrially used, like formaldehyde, methyl-tert-butyl ether (MTBE, 20%), acetic acid and dimethyl ether [1] [4–7]. Therefore, the production and use of this alcohol can be a way to reduce the fossil fuels dependence, because it could be used directly as a fuel or in fuel engine blends, with low NO_x and SO_x emissions, chemical energy carrier and as an input to produce synthetic fuels [1, 4, 5, 8] and omit partially or totally the use of non-renewable resources, in terms of the human time scale, because their quantities are finite, they fluctuate in prices, their use promotes global warming

* Corresponding author: Carlos Esteban Aristizábal Alzate

E-mail: carlosaristizabal207157@correo.itm.edu.co

ISSN 0120-6230

e-ISSN 2422-2844

and damage to the environment, so it is necessary to obtain high added value products to base the economy and consumption patterns on more sustainable activities [1, 9–11].

This article aims to simulate the catalytic conversion of SYNGAS into methanol in a packed-bed reactor. The SYNGAS gas could be obtained from the gasification of renewable sources, derived from agro-industrial residues, municipal organic waste, among others [12, 13]. Also, the SYNGAS is a useful and sustainable raw material to produce fuels, chemical commodities (urea, methanol, dimethyl ether, etc.), heat and electricity, depending on the conversion route and physicochemical treatment selected [2], [4–7], [14–16].

2. Methodology

2.1 Technology and process selected to produce methanol

The processes conventionally used to produce methanol are carried out in fixed-bed multi-tubular reactors with a CuO-ZnO-Al₂O₃ catalyst in the form of pellets and operating in the gas phase [7, 15, 17]. The catalyst CuO-ZnO-Al₂O₃ is adopted, since it is the most used on an industrial scale, it allows working in a low pressure range, it has a high selectivity for methanol production, and it reaches an excellent level of CO₂ conversion [1, 8, 18].

This heterogeneous process is highly exothermic [18, 19]. Therefore, a cooling system must be implemented, since high temperatures affect life usefulness of the catalyst bed, due to the deactivation by thermal sintering [20]. The standard technologies used in methanol synthesis are shown in Table 1.

At the industrial scale, the Lurgi-type reactor is well-known, which functions as a kind of tube and shell exchange, where the CuO-ZnO-Al₂O₃ catalyst is packed in the tubes and on the shell side, it is made circulating the cooling water [13, 19]. This configuration of catalyst packaged inside a tubular reactor is used because the process can be more controlled [21, 22], with higher conversions by catalyst weight, and ensure efficient removal of heat [1]. Besides, in this type of reactor the H₂ : CO ratio in the fed SYNGAS should be as close as 2, to maximize efficiency and yield in methanol production [14], the operating temperature should not exceed the 570 K [22], to avoid the catalyst deactivation for sintering or aging processes, which are present at high temperatures [23]. However, some studies report loss of activity starting at the range between 463.15 and 500.15 K, and becoming more rapid and severe at temperatures between 543.15 and 573.15 K [1]. This deactivation process causes the

surface area loss of the catalyst and reduction of its support area [1, 23].

Concerning pressure, this should be as high as possible, to counteract the decrease in the moles of the system by chemical equilibrium [22]. However, it should be noted, that with a high system pressure, the reactor manufacturing cost, and the energy required for SYNGAS compression are increased [23–25].

2.2 Raw material: SYNGAS

SYNGAS is a gaseous mixture obtained by gasification of carbonaceous material, such as biomass or coal. The process for SYNGAS production is called gasification, which consists in the conversion of these materials at moderate pressures and high temperatures, between 973.15 and 1473.15 K, in the presence of a gasifying or oxidizing agent, usually air, steam, or a mixture of them [26–29]. However, the quality, composition, calorific value, among other characteristics, depend on the physical and chemical properties of the biomass [30]. The characteristics of SYNGAS are shown in Table 2 and Table 3, for different types of agro-industrial biomass waste.

2.3 Math model and process simulation

The simulation of a Lurgi tube reactor operating in steady state condition is discussed. Besides, the following considerations and simplifications proposed by [18, 23, 24] are considered for this type of operation and reactor:

- Negligible radial diffusion: concentration and temperature profiles are assumed as constants, which leads to a one-dimensional model.
- Constant radial speed.
- Temperature and pressure profiles in the catalyst are assumed as constants (homogeneous catalytic particle).
- Secondary reactions are neglected due to the high selectivity of the catalyst.

The chemical kinetics used to model the methanol production process is proposed by *Vanden* [17], since it is the only one that considers the heterogeneous processes associated with the CuO-ZnO-Al₂O₃ catalyst, as noted in the comparative table of the different catalysts and chemical kinetics illustrated in [20]. Then, in Equation 1 and 2, the chemical reactions involved in the process are shown.

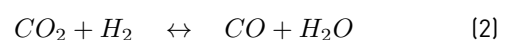
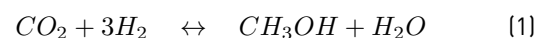


Table 1 Synthesis methanol technologies [16]

Technology	Operation temperature (K)	Operation pressure (bar)	Remarks
ICI (Syntex)	483.15-563.15	50-100	Tubular Arc Reactor with Cooling, Isothermal Linde and Toyo
Lurgi	503.15-538.15	50-100	Isothermal tubular reactor
Mitsubishi	508.15-543.15	50-200	Isothermal tubular reactor
Kellog	-	-	Spherical geometry reactor
Linde AG	313.15-543.15	50-150	-
Haldor-Topsoe	473.15-583.15	40-125	There are not commercial plants operating with this technology

Table 2 SYNGAS composition (Wet basis in % Vol.) from Colombian agro-industrial flower waste at 1,123 K for different gasifying agents. [28]

Species	Steam	Air	Air-Steam
CO (% v/v) Average	17.97	15.40	17.29
H ₂ (% v/v) Average	30.94	19.29	25.76
CO ₂ (% v/v) Average	19.61	8.34	13.94
CH ₄ (% v/v) Average	3.01	1.09	2.06
N ₂ (% v/v) Average	5.57	32.30	20.70
H ₂ O (% v/v) Average	22.90	23.59	20.26
SN	0.30	0.46	0.38

Table 3 SYNGAS composition (% Vol.) from Colombian agro-industrial waste at 1123 K for several values of steam/biomass ratio [31]

Palm matter	Steam/biomass	CO	CO ₂	H ₂	CH ₄	H ₂ O	SN
% V/V	0.50	31.15	2.31	33.97	0.94	31.63	0.95
	1.00	24.99	9.42	35.61	0.97	29.01	0.76
	1.50	20.74	13.21	36.58	0.92	28.56	0.69
	2.00	17.80	15.43	37.19	0.87	28.70	0.65
Coffee husk	Steam/biomass	CO	CO ₂	H ₂	CH ₄	H ₂ O	SN
% Wet weight	0.50	30.94	3.94	33.42	0.89	30.81	0.85
	1.00	24.80	10.69	35.12	0.90	28.49	0.69
	1.50	20.55	14.30	36.13	0.88	28.13	0.63
	2.00	17.63	16.40	36.76	0.83	28.37	0.60

Although the Lurgi technology admits pressures ranging from 50 to 100 bar, in [17] the model was developed to operate between 15 and 51 bar, and concerning temperature, this model allows working in a range between 453 and 552 K [16]. However, it has been decided to work at the maximum pressure allowed by the model, since it favors the chemical equilibrium towards the formation of methanol. Also, a 523 temperature K is used, because it is a common condition for this type of system [14] and it has been reported that catalyst deactivation occurs at temperatures above 550 K [18]. The chemical kinetics to produce methanol from catalytic conversion of SYNGAS, are illustrated in Equation 3, 4, and 5. Additionally, the Equation 5 and 6 are used to define the parameters β_n of kinetic expressions, the Equation 7 and 8 denote the kinetic constants, and Equation 9, 10, and

11 are the equilibrium constants involved in the methanol synthesis chemical reactions.

$$r_{MeOH} = \frac{k_1 f_{CO} f_{CO}^2 (1 - \beta_1)}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2} + K_{H_2} f_{H_2})^3} \quad (3)$$

$$r_{RWGS} = \frac{k_2 f_{CO_2} f_{H_2}^2 (1 - \beta_2)}{(1 + K_{CO} f_{CO} + K_{CO_2} f_{CO_2} + K_{H_2} f_{H_2})^4} \quad (4)$$

Where,

$$\beta_1 = \frac{f_M}{K_{f_1} f_{CO} f_{H_2}^2} \quad (5)$$

$$\beta_2 = \frac{f_M f_{H_2O}}{K_{f_2} f_{CO_2} f_{H_2}^3} \quad (6)$$

$$k_1 = 191.2e^{-\left(\frac{41.770}{RT}\right)} \quad (7)$$

$$k_2 = 6.392e^{-\left(\frac{60.920}{RT}\right)} \quad (8)$$

$$K_{CO} = e^{-2.902-29.640\left(\frac{1}{T}-\frac{1}{508.9}\right)} \quad (9)$$

$$K_{CO} = e^{-2.902-29.640\left(\frac{1}{T}-\frac{1}{508.9}\right)} \quad (10)$$

$$K_{H_2} = e^{-1.692+2.001\left(\frac{1}{T}-\frac{1}{508.9}\right)} \quad (11)$$

For this proposed mathematical model, r denotes the reaction rate, f fugacity, T temperature and R the ideal gas constant.

Since a reactive gaseous flow is present through a porous bed, the pressure drop along the length of the reactor is considered. Equation 12 represents this phenomenon:

$$\frac{dP}{dz} = -\frac{G}{\rho g_c D_p} * \left(\frac{1-\theta}{\theta^3}\right) \left[\frac{150 * (1-\theta)\mu}{D_p} + 1.75G\right] \quad (12)$$

Where, P is the pressure, z is the reactor length, ρ and μ are, respectively, the density and viscosity of the gas passing through the bed, D_p is the diameter of a particle forming the bed, θ is the porosity of the bed, g_c is the specific gravity and G is the surface velocity of the mass of the gas passing through the bed.

In addition, since the average and high operating temperatures are considered, the catalyst is deactivated over time by sintering or aging processes [1, 16, 23, 31]. This process is represented by Equation 13.

$$\frac{da}{dt} = -k_d * \exp\left(\frac{-E_d}{R} * \left(\frac{1}{T} - \frac{1}{T_o}\right)\right) * a^5 \quad (13)$$

Where a is the term describing the deactivation, R is the universal ideal gas constant, T is the system temperature, T_o is the reference temperature, k_d is the specific deactivation constant and is equal to $4,39 \times 10^{-5} \text{ h}^{-1}$ and E_d is the activation energy of the catalyst deactivation process and equals $9,1 \times 10^4 \text{ J/mol}$ [16].

On the other hand, the stoichiometric number (SN) is also evaluated, which is determined by Equation 14 and allows the relationship between the composition of H_2 , CO and CO_2 to be seen, since these compounds are directly related to the synthesis of methanol.

$$SN = \frac{\text{moles } H_2 - \text{moles } CO_2}{\text{moles } CO + \text{moles } CO_2} \quad (14)$$

The efficiency and performance in the methanol synthesis process are favored for SN values close to 2, with the

optimum value being 2,05 [1, 7, 16]. Values of the SN < 2 indicate a deficiency in the amount of H_2 , which causes the formation of unwanted byproducts, and an SN > 2 indicates an excess in the amount of H_2 and deficiency in carbon, this occurs when a gasification with steam, which implies a higher recirculation ratio within the reactor and a less efficient and more costly plant [16].

2.4 Model validation and simulation conditions

Initially, an algorithm is constructed in MATLAB[®], to simulate the production of methanol, from SYNGAS, which uses the mathematical model illustrated in Section 3 of this paper. The temperature variation along the reactor is not considered, since it is assumed that it operates isothermally, thanks to it is assumed the use of water as a refrigerant [18] and because it is expected to have a constant temperature, which favors the production of methanol and not drastically affecting the activity of the catalyst.

Once the algorithm is ready, it is proceeded to validate it and compare its results with references that obtain the experimental data or simulate the catalyst [CuO-ZnO-Al₂O₃] methanol production, from biomass SYNGAS. For this purpose, the following data illustrated in Table 4 and reported by [22] and [18] are used.

Table 4 SYNGAS characteristic for a methanol production. [22]

Components	Molar fraction [x]	Feed flow (mol/s/tube)
CO	0.046	
CO ₂	0.094	
H ₂	0.659	
H ₂ O	0.0004	0.639
CH ₃ OH	0.005	
N ₂	0.093	
CH ₄	0.1026	

Additionally, the methanol synthesis reactor characteristics and operation conditions, are illustrated in Table 5.

Once the model is validated, we proceed to use the compositions shown in Table 2 and provided by Sarmiento *et al.* (2015), to feed the algorithm in MATLAB[®], and thus the influence of gasifying agent in methyl alcohol chemical synthesis could be discussed. The data in Table 3 is used to determine the methanol yield production depending on the Steam/biomass ratio variation. The analysis of all results will allow establishing which of the studied residual biomasses and gasification conditions have a

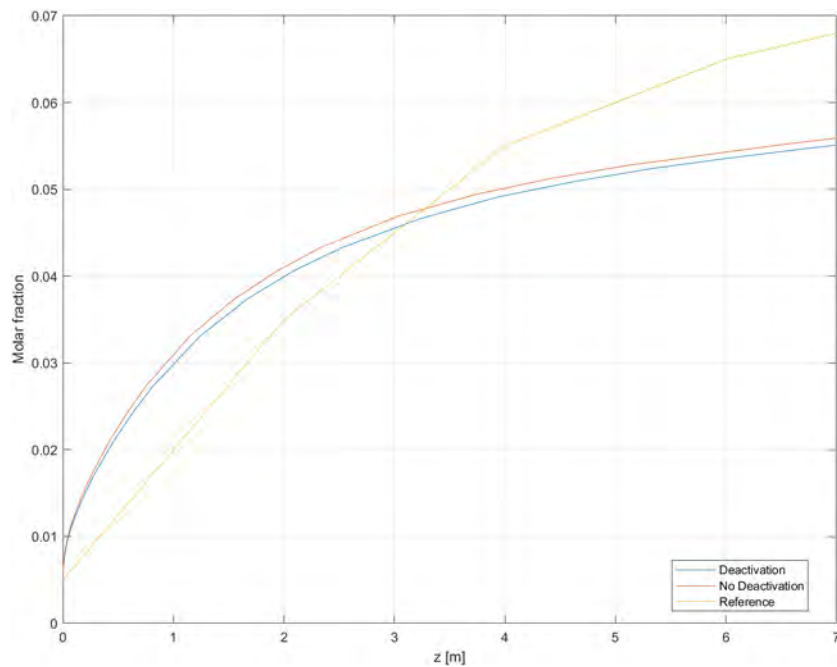


Figure 1 Comparison of methanol production for the proposed model and references [22] and [18]

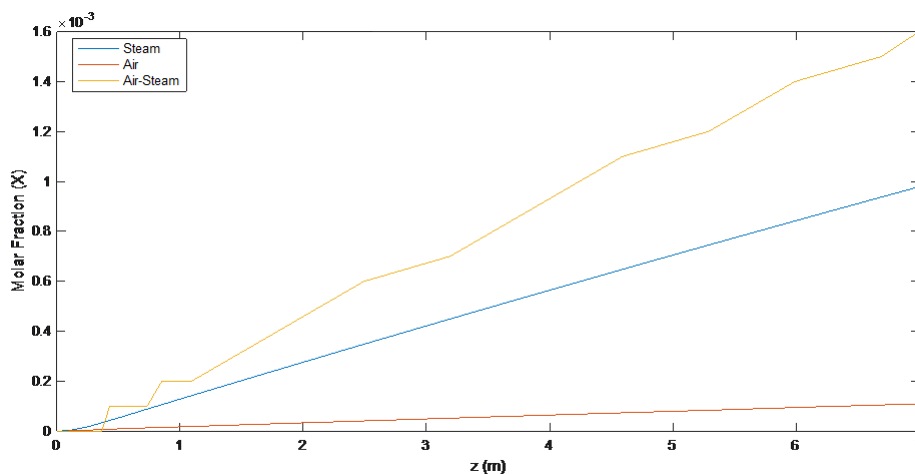


Figure 2 Methanol molar fraction profile for several gasifying agents

greater potential for obtaining a SYNGAS, according to the needs of methanol process production and the SN condition.

3. Results and discussion

3.1 Model validation

The comparison of the methanol composition profile between this model and the data reported by [22] and [18] is shown in Figure 1.

This model is suitable for the simulation for methanol

production from a SYNGAS, product of the biomass gasification because the constructed model follows the same behavior as that reported by [22]. The profile of the model results and those presented by reference show a difference for reactor lengths between 0 and 3 m, where the methanol profile for a simulated case is higher than reference results. After three meters, the trends are opposite and the reference methanol production data is higher. It is important to point out that, the model used here, considers the deactivation of the catalyst by sintering processes, whereas the one used by the reference does not.

As the catalyst deactivation rate depends on the

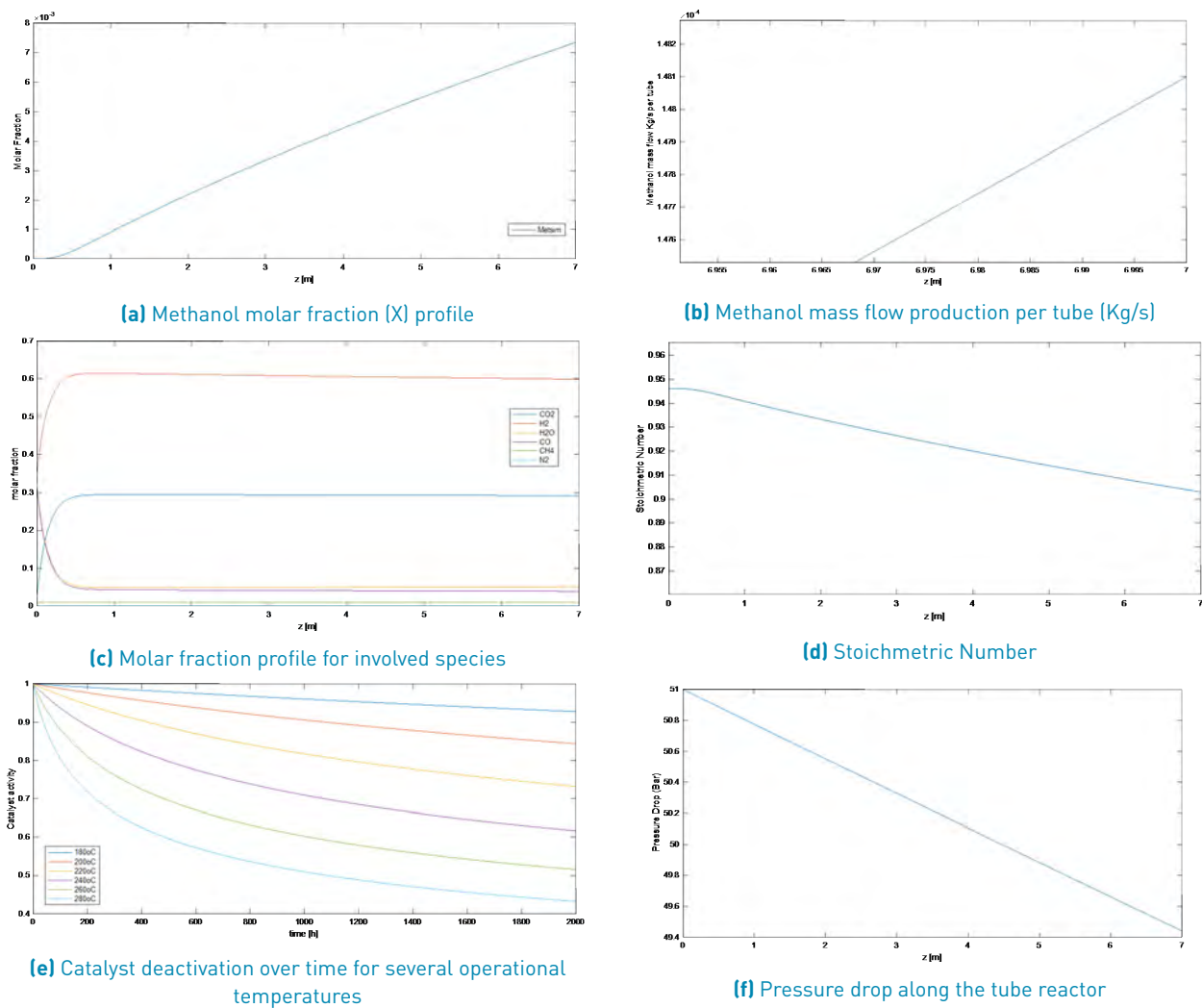


Figure 3 Simulation results for a methanol production from a palm matter SYNGAS (Steam/Biomass ratio = 2)

Table 5 Characteristics of methanol synthesis reactor. [18]

Length	7	[m]
Internal diameter (Di)	0.0341	[m]
External diameter (Do)	0.0381	[m]
Porosity	0.39	[-]
Pressure	77	[bar]
Inlet temperature	503.0	[K]
Operation temperature	523.0	[K]
Catalyst density	1,770.0	[kg/m ³]
Catalyst diameter	5.47×10^{-3}	[m]
Tubes	2,962.0	[-]

model approaches these values, from a reactor longitude between 0 to 3 m, to the reference values, which are lower, because the catalyst activity loss increases with the time and a high temperature operation.

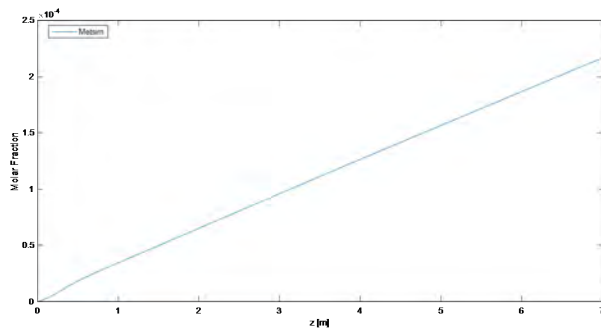
3.2 Gasification agent effect

Considering the most common, feasibility and favorable operational conditions, and that the simulations developed here are for a one catalyst packed tube, the results are then illustrated in the following figures.

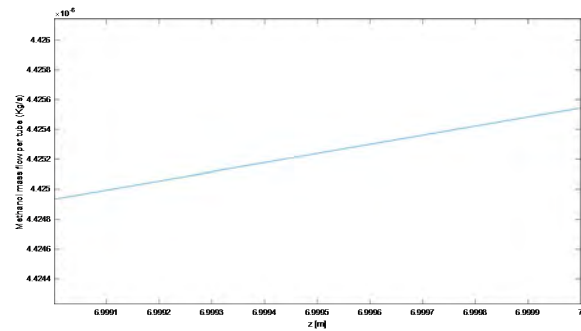
In Figure 2, it is shown the methanol molar fraction profile for SYNGAS obtained from flower waste gasification, whose compositions are shown in Table 2, which considers several gasifying agents.

temperature and system operation time, what is expected is that the methanol molar fraction for catalyst deactivation

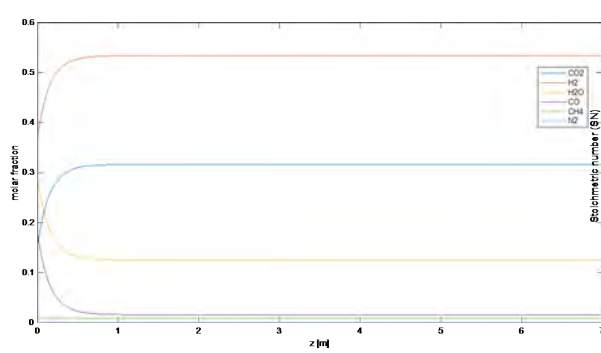
With the figure analysis, it could be said that the more adequate SYNGAS to be a raw material in a methanol



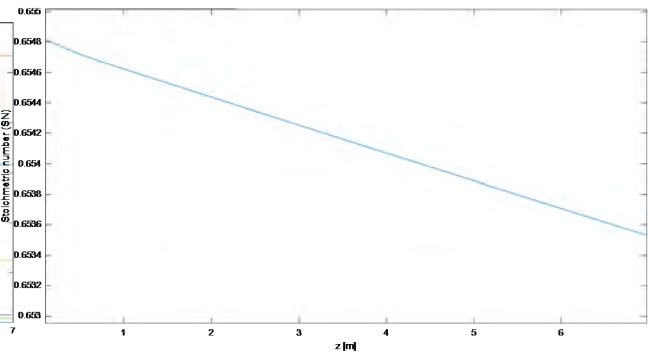
(a) Methanol molar fraction (X) profile



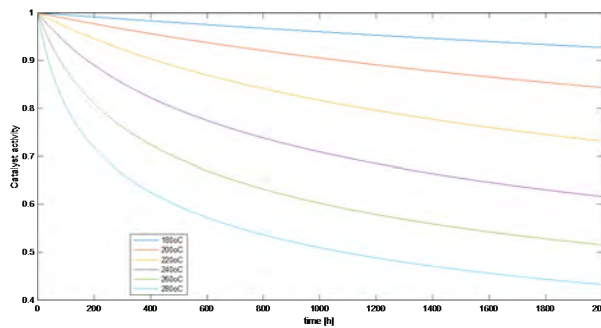
(b) Methanol mass flow production per tube (Kg/s)



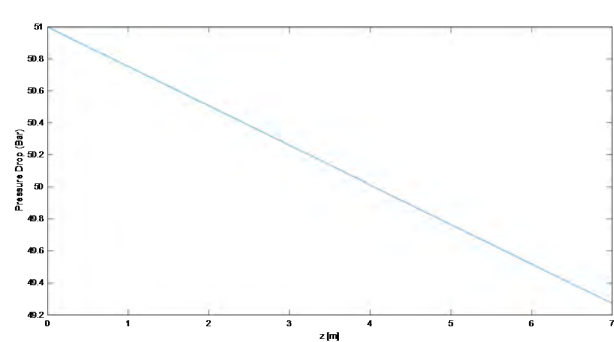
(c) Molar fraction profile for involved species



(d) Stoichiometric Number



(e) Catalyst deactivation over the time for several operational temperatures



(f) Pressure drop along the tube reactor

Figure 4 Simulation results for a methanol production from a palm matter SYNGAS (Steam/Biomass ratio = 2)

synthesis process, is derived from a gasification biomass process, which considers as a gasifying agent an air-steam mixture, followed by steam and finally, by air. The SN was the highest to air-steam, but, the methanol production was the worst because the hydrogen concentration was very low, if it is compared with the other two gasifying agents considered in this study.

Although the Nitrogen (N_2) acts like a pressurized agent to favor the chemical equilibrium towards the methanol production, its excess in the reacting gas mixture can lead to a low conversion of methanol, because the SN is low in these cases, as illustrated in Table 2. Additionally, the N_2

is not a reactant specie, therefore, it will not participate in the methanol production process; also, due to a high calorific value, it steals heat for the gasifying process.

3.3 Steam-Biomass ratio effect

The results obtained for the methanol production process simulation using a SYNGAS from Palm matter gasification and a Steam/Biomass ratio of 2.0 and 0.5, are shown in Figure 3 and Figure 4, respectively.

According to this information and comparing both results for a SYNGAS from palm matter, it can be said

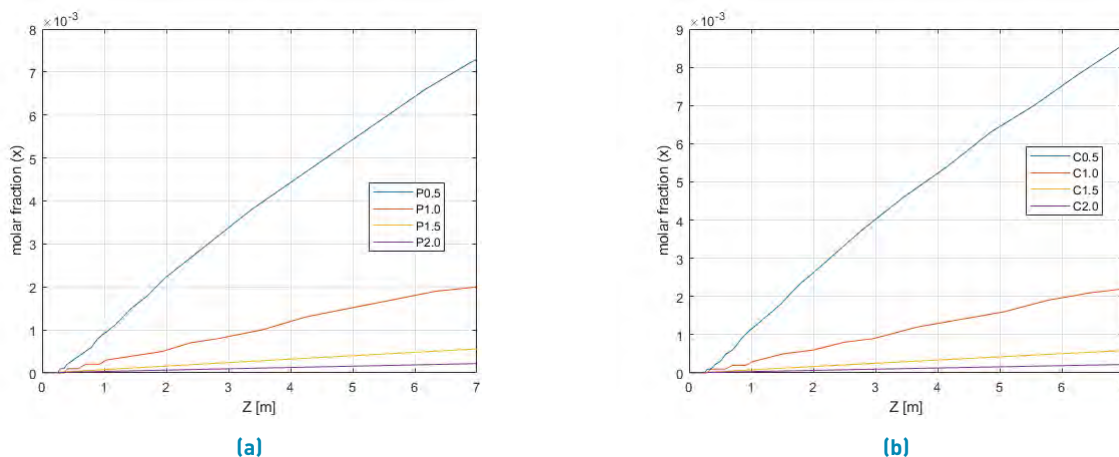


Figure 5 Evaluation of Steam/biomass ratio between 0.5 to 2.0 for two SYNGAS from Colombian biomasses steam gasification for a) Palm matter and b) Coffee husk

that with a larger Steam/Biomass ratio, smaller amounts of methanol production are reached, once the reactor longitude is achieved, with a 1.481×10^{-4} Kg/s for a S/B=0.5 and near 4.4253×10^{-6} Kg/s for a S/B=2.0.

Because the considered deactivation catalyst mechanism is sintering, it only depends on operational process temperature; thus, this parameter does not vary for the different selected biomass sources or for any other variation of operational condition.

Figure 5 shows, the methanol profile yield, for steam/biomass ratio between 0.5 until 2 for coffee husk and palm matter.

According to the results in Figure 5, the best methanol production to both evaluated biomasses are for the 0.5 biomass/steam ratio. Therefore, the methanol production yield is increased, while the Steam-biomass relationship value decreased.

3.4 Biomass selected effect

Table 6 shows the methanol results, using the selected biomass SYNGAS as a raw material. This information is useful to look for the best biomass for methanol synthesis.

Table 6 shows that the best methanol production is for the synthesis gas from the gasification of flower agro-industrial waste. Although the flower waste has the lowest stoichmetric number, these results are achieved because SYNGAS composition does not exhibit a high content of steam, and it has a higher CO₂ composition than its counterparts evaluated here.

Table 6 Methanol output molar fraction for the simulation of reference and three SYNGAS from Colombian agro-industrial waste

SYNGAS Origin	Methanol output molar fraction (X _{MetOH})
Manenti <i>et al.</i> , (2011)	5.5×10^{-2}
Flower agro industrial waste	9.8×10^{-4}
Palm matter	2.2×10^{-4}
Coffee husk	2.17×10^{-4}

4. Conclusions

A high value-added generation, through a SYNGAS catalytic conversion into methanol, is presented and discussed here. Likewise, this study considers a computational modelling, using MATLAB®, including methanol yields, operational condition evaluation, temperature and pressure, catalyst deactivation, SYNGAS composition, gasifier agent, the origin of biomass, pressure drop, among others.

The results show that the best methanol yields are achieved for the situation where the gasifier agent is pure oxygen (O₂) or steam (H₂O_(v)), being the first with a stoichmetric number near to 2. However, it is considered that producing pure O₂ is more expensive than the steam production, and biomass gasification with H₂O_(v) achieves the highest low heat value of SYNGAS. This could be explained due to the hydrogen content in the steam. Therefore, at industrial scale, it will be profitable using the steam as a gasifier agent.

The temperature and pressure are important operational parameters, because these variables are directly related

with the chemical equilibrium, chemical kinetics reactions and selectivity, but if increasing these two parameters, the initial investment, operational cost and useful life of catalyst will be affected in a negative way, all of this, without considering the origin of residual biomass and the gasifier agent identity, because the math and computational model characteristics of the catalytic process for the methanol production do not depend on these two gasifying operational conditions.

Regarding the syngas biomass origin, it can be concluded that SYNGAS with a H₂O low content is desirable, because this condition promotes the chemical equilibrium towards the methanol production. Therefore, the biomass that shows the best results is the flower agro industrial waste, because the SNGAS steam content is the lowest, if compared with coffee husk and palm matter SYNGAS, despite its SN is not the nearest to the recommended condition [2,01]. Additionally, for a good conversion of synthesis gas into methanol, it is recommended that the SYNGAS has a high hydrogen and considerable carbon dioxide amounts in the reactor inlet composition.

5. Declaration of competing interest

We declare that we have no significant competing interests including financial or non-financial, professional, or personal interests interfering with the full and objective presentation of the work described in this manuscript.

6. Acknowledgements

CEA thanks ITM to academic support and Sapiencia for the half master scholarship at the program Extendiendo Fronteras.

References

- [1] G. Bozzano and F. Manenti, "Efficient methanol synthesis: Perspectives, technologies and optimization strategies," *Prog. Energy Combust. Sci.*, vol. 56, September 2016. [Online]. Available: <https://doi.org/10.1016/j.peccs.2016.06.001>
- [2] H. W. Cooper, "Producing electricity and chemicals simultaneously," *Chem. Eng. Prog.*, vol. 106, no. 2, pp. 24–32, Feb. 2010.
- [3] A. E. Duarte, W. A. Sarache, and C. A. Cardona, "Cost analysis of the location of Colombian biofuels plants," *DYNA*, vol. 79, no. 176, pp. 71–80, 2012.
- [4] S. Leduc, J. Lundgren, O. Franklin, and E. Dotzauer, "Location of a biomass based methanol production plant: A dynamic problem in northern Sweden," *Appl. Energy*, vol. 87, no. 1, January 2010. [Online]. Available: <https://doi.org/10.1016/j.apenergy.2009.02.009>
- [5] C. N. Hamelinck and A. P. C. Faaij, "Future prospects for production of methanol and hydrogen from biomass," *Journal of Power Sources*, vol. 111, no. 1, September 18 2002. [Online]. Available: [https://doi.org/10.1016/S0378-7753\(02\)00220-3](https://doi.org/10.1016/S0378-7753(02)00220-3)
- [6] R. Rauch, J. Hrbek, and H. Hofbauer, "Biomass gasification for synthesis gas production and applications of the syngas," *Wiley Interdiscip. Rev. Energy Environ.*, vol. 3, no. 4, July 2014. [Online]. Available: <https://doi.org/10.1002/wene.97>
- [7] K. M. Holmgren, T. Berntsson, E. Andersson, and T. Rydberg, "System aspects of biomass gasification with methanol synthesis – process concepts and energy analysis," *Energy*, vol. 45, no. 1, September 2012. [Online]. Available: <https://doi.org/10.1016/j.energy.2012.07.009>
- [8] A. Bansode and A. Urakawa, "Towards full one-pass conversion of carbon dioxide to methanol and methanol-derived products," *Journal of Catalysis*, vol. 309, January 2014. [Online]. Available: <https://doi.org/10.1016/j.jcat.2013.09.005>
- [9] D. H. Meadows, *Los límites del crecimiento: informe al Club de Roma sobre el predicamento de la humanidad*. Ciudad de México, México: Fondo de Cultura Económica, 1972.
- [10] T. Damartzis and A. Zabaniotou, "Thermochemical conversion of biomass to second generation biofuels through integrated process design—a review," *Renew. Sustain. Energy Rev.*, vol. 15, no. 1, January 2011. [Online]. Available: <https://doi.org/10.1016/j.rser.2010.08.003>
- [11] P. Gangadharan, A. Zanwar, K. Zheng, J. Gossage, and H. H. Lou, "Sustainability assessment of polygeneration processes based on syngas derived from coal and natural gas," *Comput. Chem. Eng.*, vol. 39, April 06 2012. [Online]. Available: <https://doi.org/10.1016/j.compchemeng.2011.10.006>
- [12] J. H. Clark, "Green chemistry for the second generation biorefinery—sustainable chemical manufacturing based on biomass," *J. Chem. Technol. Biotechnol.*, vol. 82, no. 7, July 2007. [Online]. Available: <https://doi.org/10.1002/jctb.1710>
- [13] Z. Ravaghi and F. Manenti, "Unified modeling and feasibility study of novel green pathway of biomass to methanol/dimethylether," *Appl. Energy*, vol. 145, May 01 2015. [Online]. Available: <https://doi.org/10.1016/j.apenergy.2015.02.019>
- [14] N. L. Panwar, R. Kothari, and V. V. Tyagi, "Thermo chemical conversion of biomass – eco friendly energy routes," *Renew. Sustain. Energy Rev.*, vol. 16, no. 4, May 2012. [Online]. Available: <https://doi.org/10.1016/j.rser.2012.01.024>
- [15] A. Narvaez, D. Chadwick, and L. Kerstenbaum, "Small-medium scale polygeneration systems: Methanol and power production," *Appl. Energy*, vol. 113, January 2014. [Online]. Available: <https://doi.org/10.1016/j.apenergy.2013.08.065>
- [16] A. Riaz, G. Zahedi, and J. J. Klemeš, "A review of cleaner production methods for the manufacture of methanol," *J. Clean. Prod.*, vol. 57, October 15 2013. [Online]. Available: <https://doi.org/10.1016/j.jclepro.2013.06.017>
- [17] K. M. Vanden and G. F. Froment, "A steady-state kinetic model for methanol synthesis and the water gas shift reaction on a commercial Cu/ZnO/Al₂O₃Catalyst," *J. Catal.*, vol. 161, no. 1, June 1996. [Online]. Available: <https://doi.org/10.1006/jcat.1996.0156>
- [18] F. Manenti, F. Adani, F. Rossi, G. Bozzano, and C. Pirola, "First-principles models and sensitivity analysis for the lignocellulosic biomass-to-methanol conversion process," *Comput. Chem. Eng.*, vol. 84, January 04 2016. [Online]. Available: <https://doi.org/10.1016/j.compchemeng.2015.05.012>
- [19] S. Yusup, N. Phuong, and H. Zabiri, "A simulation study of an industrial methanol reactor based on simplified steady-state model," *Int. J. Res. Rev. Appl. Sci.*, vol. 5, no. 3, pp. 213–222, Dec. 2010.
- [20] N. Couto, A. Rouboa, V. Silva, E. Monteiro, and K. Bouziane, "Influence of the biomass gasification processes on the final composition of syngas," *Energy Procedia*, vol. 36, 2013. [Online]. Available: <https://doi.org/10.1016/j.egypro.2013.07.068>
- [21] F. Manenti, S. Cieri, and M. Restelli, "Considerations on the steady-state modeling of methanol synthesis fixed-bed reactor," *Chem. Eng. Sci.*, vol. 66, no. 2, January 15 2011. [Online]. Available: <https://doi.org/10.1016/j.ces.2010.09.036>
- [22] H. S. Fogler, *Elementos de ingeniería de las reacciones químicas*. Madrid, Spain: Pearson Educación, 2001.
- [23] O. Levenspiel, *Ingeniería de las reacciones químicas*, 1st ed. Barcelona, España: Editorial Reverté, S.A, 2005.
- [24] M. Iborra, J. Tejero, and F. Cunill. (2013) *Reactores multifásicos*. [Online]. Available: <http://diposit.ub.edu/dspace/bitstream/2445/>

- 33262/1/APUNTES%20RM.pdf
- [25] T. R. Pacioni and *et al.*, "Bio-syngas production from agro-industrial biomass residues by steam gasification," *Waste Manag.*, vol. 58, December 2016. [Online]. Available: <https://doi.org/10.1016/j.wasman.2016.08.021>
- [26] M. Prakash, A. Sarkar, J. Sarkar, S. S. Mondal, and J. P. Chakraborty, "Proposal and design of a new biomass based syngas production system integrated with combined heat and power generation," *Energy*, vol. 133, August 15 2017. [Online]. Available: <https://doi.org/10.1016/j.energy.2017.05.161>
- [27] A. Sarmiento, D. Maya, F. Chejne, and E. Lora, "Gasification of agro-industrial wastes for electricity cogeneration," in *ASME Turbo Expo 2015: Turbine Technical Conference and Exposition*, Quebec, Canada, 2015, pp. 1–7.
- [28] S. Ramirez, F. E. Sierra, and C. A. Guerrero, "Gasification from waste organic materials," *Ing. e Investig.*, vol. 31, no. 3, pp. 17–25, Sep. 2011.
- [29] R. Rodrigues, A. R. Muniz, and N. R. Marcilio, "Evaluation of biomass and coal co-gasification of brazilian feedstock using a chemical equilibrium model," *Brazilian J. Chem. Eng.*, vol. 33, no. 2, April 2016. [Online]. Available: <https://doi.org/10.1590/0104-6632.20160332s00003479>
- [30] L. E. García, "Obtención de gas combustible a partir de la gasificación de biomasa en un reactor de lecho fijo," M.S. thesis, Universidad Nacional de Colombia, Bogotá, Colombia, 2011.
- [31] K. Ibsen, "Equipment design and cost estimation for small modular biomass systems , synthesis gas cleanup , and oxygen separation equipment task 2: Gas cleanup design and cost equipment design and cost estimation for small modular biomass systems , synthesis gas cl," National Renewable Energy Laboratory, San Francisco, CA, USA, Tech. Rep. NREL/SR-510-39945, May 2006.