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Modelling and Simulation of Methanol and Biodiesel Production Processes using Innovative Technologies

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Biodiesel is considered to be a promising alternative or additive to fossil fuel. Biodiesel, fatty acid methyl esters (FAME), is produced by transesterification of triglycerides or fatty acids with alcohols (i.e. methanol or ethanol, in the presence of a suitable acidic or alkaline catalyst. The present work is focused on process modelling and simulation of biodiesel production using: *i)* an innovative method for methanol synthesis, methanol being an important raw-material for biodiesel, as well as *ii)* an intensified method for biodiesel production (i.e. reactive distillation – RD). Methanol production from CO_2 and H_2 is considered to be an interesting method for CO_2 utilization. The main advantages of this method are the reduction of greenhouse gas emissions and the production of one valuable chemical, methanol. The H_2 for the methanol synthesis is obtained from wood chips through chemical-looping gasification. Beside methanol, other raw-materials for biodiesel production are triglycerides and the catalyst. The classical acid method, consisting in reaction and separation, and the intensified method based on RD for biodiesel production are investigated and compared from technical and environmental point of view. The study also considers as benchmark cases biodiesel production using classical and intensified methods, methanol deriving from syngas, syngas being obtained from natural gas (NG) steam reforming (SR). A productivity of 100,000 t/year of biodiesel is set for all cases. Purities higher than 99% are obtained both for the main product, biodiesel, and for the by-product, glycerol. The results of the simulations lead to the conclusion that RD for biodiesel production gives superior performance in terms of raw materials consumption, biodiesel purity, by-product flow-rate and CO_2 emissions but energy and steam consumption should be reduced in order to make this technology competitive at industrial scale.

1. Introduction

A sustainable future calls for sustainable fuels. A percentage of 30% of the total greenhouse emissions drives from the transportation sector with CO_2 being the main contributor (Awad et al., 2018). The best way to reduce the CO_2, CO and NO_x emissions is to use sustainable fuel alternatives such as biodiesel (Erdiwansyah et al., 2019). Biodiesel sustainability depends on feed stocks, the character of lands for bioenergy crops and the production process (Piemonte et al., 2014). Biodiesel production in 2017 was around 36 billion liters with the European Union generating 13.5 billion liters of biodiesel (OECD-FAO, 2018). The most relevant methods for biodiesel production are: pyrolysis, transesterification, dilution and usage of supercritical methanol. The advantages and disadvantages of the above mentioned methods, the conditions involved in each case as well as a classification of transesterification is offered by Atabani and co-authors (Atabani et al., 2012). Methanol, as well, can be generated starting from various feed stocks (i.e. natural gas, coal, heavy oil) and using various technologies (i.e. reforming, gasification). In the last decade the attention was focused on methanol production from renewable sources. Green methanol can be produced from CO_2 and H_2. In order to be green H_2 should be generated from water electrolysis using wind, solar or biomass electricity. Other green technologies for H_2 generation are: biomass pyrolysis or steam/oxygen gasification and reforming of biomass-derived products (Bozzano and Manenti, 2016). CO_2 can be captured from energy intensive processes (i.e. cement, steel, chemical or power generation plants) reducing in this way their emissions into the atmosphere. The novelty of the present research consists on the comparison between classical method of biodiesel production and the

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intensified one based on RD, biodiesel being produced from two different sources, a fossil fuel source (i.e. NG) and a renewable one (i.e. biomass).

2. Plants configurations and models assumptions

The cases investigated in the present paper are presented in Table 1.

Table 1: Cases investigated in the present research

Case name	Final product	Technology for biodiesel production	Intermediate Key component	Raw-material for intermediate key component production	Technology for converting the raw-material into intermediate key component
Case 1	Biodiesel	Classic	Methanol	NG	Steam reforming
Case 2	Biodiesel	Intensified	Methanol	NG	Steam reforming
Case 3	Biodiesel	Classic	Methanol	Biomass	Chemical-looping gasification
Case 4	Biodiesel	Intensified	Methanol	Biomass	Chemical-looping gasification

Classic - reaction and separation for biodiesel production, Intensified – RD for biodiesel production

Case 1 refers to biodiesel production by means of classical method using NG as raw-material, Case 2 refers to biodiesel production by means of intensified method using NG as raw-material; Case 3 is represented by biodiesel production through classical method using biomass as raw-material and Case 4 is the biodiesel production by means of intensified method using biomass as raw-material. Methanol is the intermediate key component for all cases. Methanol production from syngas, which is obtained from NG by SR, is a common part for the first two cases. In the latter cases methanol production from CO_2 and H_2 were considered, CO_2 and H_2 being obtained from biomass through chemical-looping gasification technology. Biomass-derived chemical-looping gasification is a novel technology to convert biomass into renewable hydrogen-enriched syngas (Hu et al., 2020). All cases were modeled using ChemCAD and Aspen Plus software packages.
Most methanol industrial processes use syngas as raw material, syngas being produced from different fossil fuels. In the present study syngas is obtained from NG. Methanol production process from syngas is presented in Figure 1A while methanol production process from CO_2 and H_2 is presented in Figure 1B.

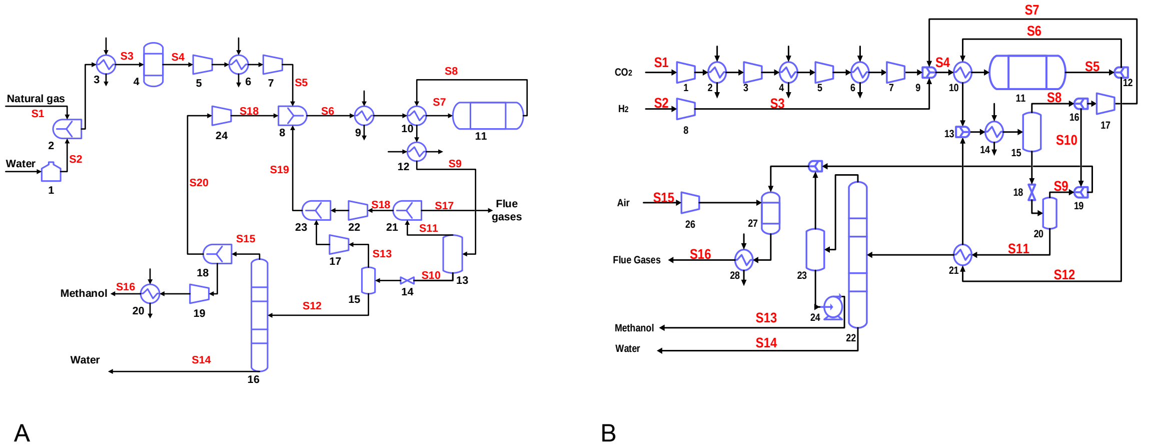

Figure 1: A) Methanol production from syngas derived from NG (sub process for Case 1 and Case 2)
B) Methanol production from CO_2 & H_2 derived from biomass (sub process for Case 3 and Case 4)

NG, stream S1 is converted to syngas in the SR technology. Syngas, S4, is compressed to 108 atm, in a two-stage compressor with intermediate cooling, furthermore mixed with two recycled streams, S18 and S19, and preheated up to the reactor inlet temperature. The reactions occurring in the methanol production are:

$$CO \quad + \quad 2H_2 \quad \leftrightarrow \quad CH_3OH \qquad (1)$$

$$CO_2 \quad + \quad 3H_2 \quad \leftrightarrow \quad CH_3OH \quad + \ H_2O \qquad (2)$$

The output stream of the reactor, S8, leaves the reactor at 267°C and enters the heat exchanger (Unit 10) which is used to preheat the reactor inlet flow. After this thermal integration, the flow is cooled down to 38°C. The liquid and gaseous phases are separated using a separator (Unit 13). S11 is divided into two streams, S18, which is compressed and recycled, and S17 which is removed from the system as a purge. The liquid phase, S10, is sent to another separation unit to remove the remaining gases and then fed to the distillation column (Unit 16). Methanol is obtained in the top of the column, as S16, whilst water, collected at the bottom, can be used to generate the steam required in the syngas production.

The methanol production process from CO_2 and H_2 is presented in Figure 1B. CO_2 feed, S1, is compressed up to 78 atm through a four-stage compressor with intermediate cooling. H_2 feed stream, S2 is also compressed to the same pressure. Compressed raw-materials streams are mixed with the recycle stream, S7, and fed to the heat exchanger (Unit 10), where they are heated up to reach the reactor inlet temperature, 210°C. S5 from the reactor is divided into two streams one is used to preheat the reactor feed, while the other is used to preheat the column feed. After heat integration, the streams are mixed again and cooled down to 35°C and then separated in two gas-liquid separators (Unit 15 and Unit 20). The liquid stream, S11, is preheated and sent to the distillation column, Unit 22. Liquid methanol is obtained in S13.

Hydrogen requested for methanol synthesis can be obtained from biomass using gassification or chemical-looping gassification technologies. Gasification of biomass and production of high yields of clean syngas is very challenging (Volpe et al., 2016). Chemical-looping gasification is a promising technology that uses two interconnected fluidized bed reactors with a solid oxygen carrier circulating between them (see Figure 2). In the first reactor (i.e. fuel reactor) gassification of biomass takes place using oxygen from the oxygen carrier and steam as gassifying agent, while in the second reactor (i.e. air reactor) the oxygen carrier is regenerated.

Compared to other gassification technologies, chemical-looping gasification presents some advantages (Ge at al., 2016), such as: i) no nitrogen dillution leading to higher quality syngas as well as minimizing the energy penalty of CO_2 separation, ii) lower enegy penalty by removing the air separation unit (ASU) used for O_2 production, iii) autothermal operation – heat for endothermic gasification and reduction reactions supplied by the oxygen carrier returning from the air reactor. The proposed hydrogen production technology, represented in Figure 3, was simulated using Aspen Plus software package. The main characteristics of biomass used for chemical-looping gasification as well as the design assumptions of this technology are listed in Table 2.

Table 2: Main design and modelling assumptions for hydrogen production from biomass

Process Unit	Assumption
Ultimate and Proximate analyses of wood chips (Pala et al., 2017)	Moisture (wt.%): 20.00. Proximate analysis (wt.% dry): volatile matter – 80; fixed carbon - 18.84; ash - 1.16. Ultimate analysis (wt.% dry): C - 51.19; H - 6.08; O - 41.30; N - 0.20; S - 0.02; Cl - 0.05; Ash - 1.16.
Chemical-looping gasification	Property method: PR with BM modification; Tar formation notconsidered; Operating conditions: P = 1 atm; T_{AR} = 950°C; T_{FR} ≈ 800°C; Oxigen carrier: Ilmenite (0.50 wt.% Fe_2O_3 + 0.50 wt.% TiO_2) Fluidization agent: Steam at 150°C , 1 atm.

AR – Air reactor; FR – Fuel reactor; PR- Peng-Robinson; BM – Boston-Mathias

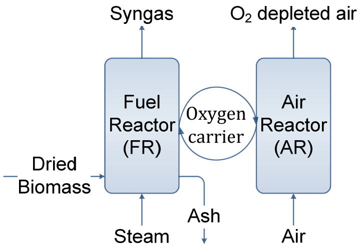

Figure 2: Chemical-looping gasification of biomass

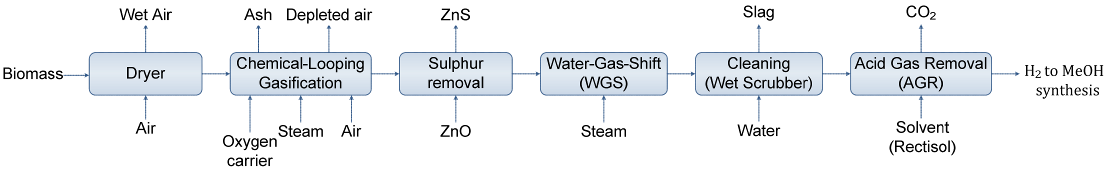

Figure 3: Conceptual design of hydrogen production from biomass

Biodiesel is produced via a transesterification reaction, in which triglycerides react with a primary alcohol to generate two products. The main product is the fatty acid methyl ester (FAME) or methyl oleate, while glycerol is obtained as a by-product. Figure 4 illustrates the process flow diagram for biodiesel production process through the classic method.

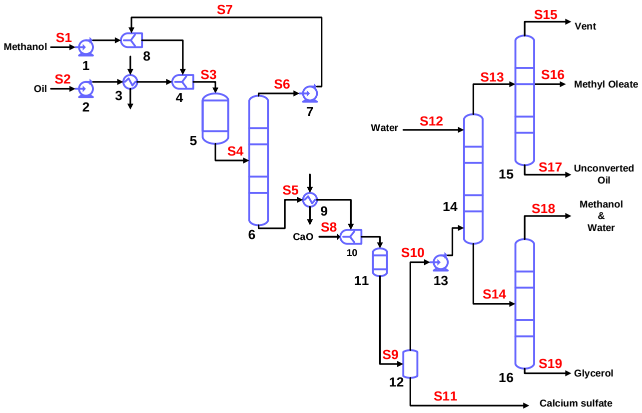

Figure 4: Biodiesel production through classic method (sub-process for Case 1 and Case 3)

Methanol, oil (i.e. rapeseed oil) and sulfuric acid feed streams are all brought to a pressure of 4 atm and mixed before entering the transesterification reactor, Unit 5. A distillation column, Unit 6, installed after the transesterification reactor, aims to separate and recycle the unconverted methanol S7. The residue from the column, S5, is cooled down to 60°C and mixed with calcium oxide (S8) in order to neutralize the catalyst (i.e. H_2SO_4); the resulting calcium sulfate is removed from the system in Unit 12. The mixture is sent to an extraction column (Unit 14) and washed with water, S12, separating the biofuel and the unconverted triglyceride from methanol and glycerol. S13 stream, containing biofuel and unconverted triglyceride, is sent into another distillation column (Unit 15). Biodiesel is obtained in stream S16. The water, glycerol and methanol mixture that is obtained after the extraction step is separated in a third distillation column (Unit 16). The water-methanol mixture leaves the column at the top, while glycerol is recovered at the bottom, S19. As mentioned before, biodiesel production process was also modelled following an innovative method, RD. Instead of Unit 5 and Unit 6 from Figure 4 a single column containing a reaction zone was used. In RD both reaction and separation occur in the same unit. Beside the reaction and separation sections, the process follows the same path as described in Figure 4. The main design assumptions considered in the present study are summarized in Table 3.

Table 3: Main design assumptions for various sub-processes involved in Cases 1 – 4

	Modelling and simulation details and main design assumptions
Methanol from syngas, syngas from NG	Raw materials: natural gas, water; Main product: methanol; By-product: flue gases, water; Thermodynamic package used: SRK; Assumptions: reactor isothermal 267°C; distillation column 42 stages; distillate component mole fraction 0.99 CH_3OH, bottom component mole fraction 0.001 CH_3OH; HE min ΔT 10˚C.
Methanol from CO_2 and H_2, CO_2 and H_2 from biomass gasification	Raw materials: CO_2, H_2, air; Main product: methanol; By-product: flue gases, water; Thermodynamic package used: UNIFAC; Assumptions: methanol reactor isothermal 210°C; distillation column 57 stages, distillate component recovery 99.75% CH_3OH, bottom component recovery 99.75% H_2O; compressors efficiencies 75%; pump efficiency 75%; HE min ΔT 10˚C.
Biodiesel through classic method (reaction & separation)	Raw materials: methanol, triglyceride, sulphuric acid, water, calcium oxide; Main product: biodiesel; By-products: glycerol, unconverted triglyceride; Thermodynamic package used: UNIFAC; Assumptions: transesterification kinetic reactor thermal mode isothermal 60°C; methanol recovery column 10 stages, RR 2, bottom component recovery 93.25% glycerol; extraction column 4 stages; biodiesel column 18 stages, top pressure 0.40 atm, RR 4, bottom component recovery 98.90% monoolein; glycerol distillation column 6 stages, RR 2, bottom product temperature 107.30°C; pump efficiencies 75%; HE min ΔT 10˚C.
Biodiesel through innovative method (RD)	Raw materials: methanol, triglyceride, sulphuric acid, water, calcium oxide; Main product: biodiesel; By-products: glycerol, unconverted triglyceride; Thermodynamic package used: UNIFAC Assumptions: reactive distillation column 30 stages, feed stages no. 8 and 19, RR 2, reaction volume stages 8 -16; extraction column 4 stages; biodiesel column 18 stages, RR 4, bottom component recovery 99% monoolein; glycerol column 6 stages, RR 2, bottom product temperature 107.3°C; pump efficiency 75%; HE min ΔT 10˚C.

HE – heat exchangers, RR – reflux ratio, UNIFAC – UNIQUAC Functional-group Activity Coefficients; SRK – Soave Redlich Kwong

The transesterification reaction occurring either in the transesterification reactor or RD column were modelled using kinetic rate expressions for the forward and backwards reactions (Giwa and Ogunware, 2018). The parameters involved in the expressions are presented in Table 4.

Table 4: Kinetic data for the transesterification reaction of triolein with methanol

Reactions	Expressions for reaction rate	Parameters	
		k (mol^{-1}litre min^{-1})	E (cal/kmol)
$C_{57}H_{104}O_6 + CH_3OH \rightarrow C_{39}H_{72}O_5 + C_{19}H_{36}O_2$	$r_1=k_1*C_{Triolein}* C_{Methanol}$	1.469×10^8	14,040
$C_{39}H_{72}O_5 + C_{19}H_{36}O_2 \rightarrow C_{57}H_{104}O_6 + CH_3OH$	$r_2= k_2 * C_{Diolein} * C_{Methyl\ oleate}$	105,100	10,739
$C_{39}H_{72}O_5 + CH_3OH \rightarrow C_{21}H_{40}O_4 + C_{19}H_{36}O_2$	$r_3= k_3* C_{Diolein}* C_{Methanol}$	1.19×10^{10}	16,039
$C_{21}H_{40}O_4 + C_{19}H_{36}O_2 \rightarrow C_{39}H_{72}O_5 + CH_3OH$	$r_4= k_4* C_{Monoolein}* C_{Methyl\ oleate}$	1.725×10^8	13,907
$C_{21}H_{40}O_4 + CH_3OH \rightarrow C_3H_8O_3 + C_{19}H_{36}O_2$	$r_5= k_5* C_{Monoolein}* C_{Methanol}$	2.55×10^{10}	7,173
$C_3H_8O_3 + C_{19}H_{36}O_2 \rightarrow C_{21}H_{40}O_4 + CH_3OH$	$r_6= k_6* C_{Glycerol}* C_{Methyl\ oleate}$	627,700	10,997

Triolein – $C_{57}H_{104}O_6$; Diolein – $C_{39}H_{72}O_5$; Monoolein – $C_{21}H_{40}O_4$; Methyl oleate – $C_{19}H_{36}O_2$; Glycerol – $C_3H_8O_3$

3. Results and discussions

Based on mass and energy balances different key performance indicators were calculated and summarized in Table 5. The productivity, for all cases, was fixed at 13,333.33 kg/h of biodiesel.

Analyzing the data presented in Table 5 it can be noticed that the NG flow-rate used for biodiesel production (e.g. 837.92 kg/h for Case 1 and 1,043.75 kg/h for Case 2) is lower than the biomass flow-rate used to generate the same quantity of biodiesel (e.g. 2,843.48 kg/h for Case 3 and 3,541.66 kg/h for Case 4). It can be also noticed that steam consumption is higher in the NG cases compared to biomass cases. From environmental point of view the NG cases will have a higher impact due to the higher steam and energy consumption. Even if the CO_2 emissions in the biomass cases are higher compared to NG cases these emissions will end up in biomass growing, lowering the environmental impact of Case 3 and Case 4 compared to Case 1 and Case 2. The innovative reactive distillation method (Case 2 and Case 4) requires smaller quantities of methanol (e.g. 36,644.48 kg/h for Case 2 and 38,854.51 kg/h for Case 4) compared to the classical method (Case 1 and Case 3).

Table 5: Technical comparison among Cases 1 – 4

Parameter	Units	Case 1	Case 2	Case 3	Case 4
NG	kg/h	837.92	1,043.75	-	-
Biomass	kg/h	-	-	2,843.48	3,541.66
Methanol fresh	kg/h	1,531.31	1,907.40	1,531.31	1,907.40
Methanol recycle	kg/h	37331.21	34737.08	37331.21	36947.11
Methanol total	kg/h	38,862.52	36,644.48	38,862.52	38,854.51
Triglyceride	kg/h	21,428.00	20,990.20	21,428.00	20,990.20
Sulphuric acid	kg/h	3,072.57	3,009.79	3,072.57	3,009.79
Glycerol	kg/h	18.25	41.62	18.25	35.17
Biofuel purity	%	99.31	99.41	99.31	99.41
Glycerol purity	%	99.77	99.43	99.77	99.37
Total CO_2 emissions	kg/h	1,431.95	1,425.17	1,813.69	1,805.65
Total Energy consumption	kW	1,373.98	4,530.98	1269,96	4,540.83
Total Steam consumption	kg/h	65,896.17	89,101.48	63,279.20	87,070.57

This conclusion is the same also for the other raw-materials, triglyceride and sulfuric acid. For instance the quantity of triglyceride used in the RD method is 20,990.20 kg/h (for Case 2 and Case 4) lower than the flow-rate of triglyceride used in the classical biodiesel production process cases (e.g. 21,428.00 kg/h). The highest purities for biofuel are obtained in RD cases, Case 2 and Case 4, (e.g. 99.41%). The purities of biofuel obtained in classical method, Case 1 and Case 3, are lower than the purities of biofuel based on RD but higher than 99%. Glycerol is the by-product obtained in biodiesel process. The highest quantities of glycerol produced in the biodiesel process are obtained in Case 2 (e.g. 41.62 kg/h), followed by Case 4 (e.g.35.17 kg/h). This glycerol can be furthermore converted into methanol and recycled back to the transesterification reactor. By using this approach the quantity of fresh methanol introduced into the system, and the quantities of natural gas (NG) and biomass used for methanol production will be lower compared to the values presented in Table 5. The total CO_2 emissions are also lower in the RD case compared to the classical case. The positive aspects of RD mentioned above are not reflected anymore in the energy and steam consumption. The energy consumption for RD is about 3.3 times higher than the energy consumption of classical method when NG is used for biodiesel production (Case 2 vs. Case1) and about 3.6 times higher when biomass is converted to biodiesel (Case 4 vs. Case 3). The steam consumption is also higher, about 1.35 times, in the RD case compared to classical method.

4. Conclusions

The present paper evaluates biodiesel production from NG and biomass using the traditional method, consisting on reaction followed by separation but also a novel process based on RD. The technical parameters outline reduced raw-materials consumption, as well as improved biofuel purity for the reactive distillation method compared to the classical method. The biofuel purity obtained in RD cases is 99.41%. The energy consumption and steam consumption are higher in the RD cases compared to classical method. Consequently, the method can to be efficient and its implementation on industrial scale can represent an attractive prospect if the energy consumption and steam consumption will be reduced.

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References

Atabani A.E., Silitonga A.S., Badruddin I.A., Mahlia T.M.I., Masjuki H.H., Mekhilef S., 2012, A comprehensive review on biodiesel as an alternative energy resource and its characteristics, Renewable and Sustainable Energy Reviews 16, 2070-2093.

Awad O.I., Mamat R., Ibrahim T.K., Hammid A.T., Yusri I.M., Hamidi M.A., Humada A.M., Yusop A.F., 2018, Overview of the oxygenated fuels in spark ignition engine: Environmental and performance, Renewable and Sustainable Energy Reviews, 91, 394-408.

Bozzano G., Manenti F., 2016, Efficient methanol synthesis: Perspectives, technologies and optimization strategies, Progress in Energy and Combustion Science, 56, 71-105.

Erdiwansyah, M. R., Sani M.S.M., Sudhakar K., Kadarohman A., Sardjono R.E., 2019, An overview of Higher alcohol and biodiesel alternative fuels in engines, Energy reports, 5, 467-479.

Giwa A., Ogunware M.A., 2018, Modelling, Simulation and Control of a Reactive Distillation Process for Biodiesel Production, ABUAD Journal of Engineering Research and Development, 1, 49-60.

Hu Q., Shen Y., Chew J.W., Ge T., Wang C.H., 2020. Chemical looping gasification of biomass with Fe_2O_3/ CaO as the oxygen carrier for hydrogen-enriched syngas production, Chemical Engineering Journal, 379.

OECD-FAO, 2018, <http://www.fao.org/3/I9166EN/I9166EN.pdf> accessed 10 November 2019

Pala L.P.R., Wang Q., Kolb G., Hessel V., 2017, Steam gasification of biomass with subsequent syngas adjustment using shift reaction for syngas production: An Aspen Plus model, Renewable Energy, 101, 484-492.

Piemonte V., Di Paola L., Gentile A., Masciocchi B., Russo V., Iaquaniello G., 2014, Biodiesel Production from Microalgae: Ionic Liquid Process Simulation, Chemical Engineering Transactions, 39, 379-384.

Volpe R., Messineo S., Volpe M., Messineo A., 2016, Catalytic Effect of Char for Tar Cracking in Pyrolysis of Citrus Wastes, Design of a Novel Experimental Set Up and First Results, Chemical Engineering Transactions, 50, 18-186.