Aspen plus simulation of sargassum for quality synthesis gas

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ABSTRACT

Biomass is widely considered as a raw material for the production of biochemicals and biofuels and among all the options for its use, the gasification process is the most popular due to its environmental advantages. The great arrival of sargassum to the coasts of the State of Quintana Roo, Mexico, which has taken place for several years, forces us to study its energy use. In this study, the experimental results of the gasification of four biomasses (pine sawdust, bamboo dust, rice husk, and cane bagasse) from three different bibliographical references were simulated and validated, using the Aspen Plus computer software. The simulation model used considers the combustion of 30% of the biomass and therefore an energy balance, in addition to an estimate of the tar generated in the process. Based on the comparison of the percentage molar composition and the heating value of the syngas obtained the performance of the process was evaluated, where the lowest error per difference was for the validation of rice husk (RH) with an ER of 0.35. Subsequently, the sargassum gasification simulation was carried out with information on the properties of this biomass from five bibliographic references, obtaining as a result a syngas with a lower heating value (LHV) that varies between 2.6 and 4.8 MJ/Nm^3 for ER of 0.3 and 0.35, respectively.

1. Introduction

1.1. Contextualization

The interest in the use of renewable energy has increased in recent years, due to worrying factors such as the depletion of fossil reserves, the increase in energy consumption and in greenhouse gas emissions and global warming. Among all the alternative energy sources, the use of biomass is increasing rapidly for energy production, this is due to the fact that it constitutes a closed carbon cycle, this means that using biomass reduces the CO_2 that is sent to the atmosphere, since that part of it has been absorbed during the growth of the plants that were previously used to produce it. Biomass can be used as a feedstock to produce transportation fuels and bio-chemicals and also heat and power.

Biomass gasification has technical and economic limitations (such as the formation of tar) for its large-scale commercialization and industrialization, so biomass gasification has been analyzed and studied experimentally and through modeling and simulations.

Experiments can provide more reliable design data than can be obtained through modeling or simulation, but they are more expensive, which is why computational fluid dynamics models have been used by different types of software (Aspen Plus, Aspen Hysys, etc.). Chemkin, Fluent and Open-Foam) to simulate biomass gasification. This simulation or mathematical modeling of the gasifiers

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provides a qualitative guide on the effect of the design and the operational results or the power parameters necessary for its operation can be obtained [1].

Although there are several researchers who have studied biomass gasification using the Aspen Plus simulator [2–7], there are few papers on biomass gasification considering tar forman ion[8], and even fewer published on the gasification of the biomass studied in this work (sargassum). For this reason, the objective of this study is to validate a gasification model, already developed previously [9], for its use in different gasification technologies, which consists of six stages (biomass feeding, drying, pyrolysis, combustion, heterogeneous reactions and gasification), this through the use of Aspen Plus to simulate the syngas content produced from gasification to later simulate the gasification of sargassum. Biomass gasification from three different literature references was studied, as well as the variation of the syngas composition and higher heating value (HHV) of the reported experiments.

On the other hand, pelagic Sargassum, commonly known as sargassum, is a floating dun or brown macroalgae found in an area of the Atlantic Ocean known as the Sargasso Sea. It is known that marine currents and winds cause large landslides of this sea, which are then driven to drift, arriving massively on the coasts of the State of Quinta Roo, Mexico [10]. The massive arrival of sargassum has had negative effects; at an ecological level: massive accumulation on the beaches (with some dead animals), interference with nesting and hatching of turtles, mortality of seagrasses near the coast, eutrophication, accumulation of organic waste on the sea coast, mortality of fish for hypoxia (lack of sufficient oxygen in the tissues to maintain body functions), and interruption of the transit of species and changes in coastal ecosystems [11]. At the level of environmental impact: loss of transparency of the water, of the turquoise blue color and of beaches as a tourist attraction, emission of harmful substances, mainly hydrogen sulfide (H_2S), due to the rapid decomposition of sargassum, generation of bad odors and unhealthy environments. And at an economic level: losses in tourism and impact on service providers [11].

These effects make it necessary to study the gasification of sargassum and the quality of its syngas as a potential biofuel that can be used energetically. In order to establish quality parameters of said gas, this work proposes to use 30% of the heating value of biomass in the combustion stage to self-maintain the system [1], estimate the lower heating value (LHV) and the generation of tars, among the main parameters.

1.2. Gasification conditions

Biomass gasification is a complex multi-step thermochemical process that operates in a temperature range of 600 to 1500 °C [2]. The syngas obtained is mainly composed of H_2, CO, CO_2 and small amounts of light hydrocarbons and other pollutants. The concentration of each gas species depends mainly on factors such as the gasification parameters, the chemical composition of the biomass and the design of the plant.

1.2.1. Parameters of gasification

Among the parameters of gasification, this work considers the physical-chemical properties of biomass, biomass moisture content, temperature, pressure, gasification medium, and equivalence ratio (ER).

The gasification outlet temperature and pressure are considered to be between 600 and 900 °C, as very high pressures present difficulties with respect to feeding pressurized biomass and higher temperatures cause melting and sintering of the ashes, which are not suitable for stable operation of the gasifier [2].

As gasification media, four can be used: air, carbon dioxide, steam and a mixture of steam and oxygen; depending on the medium used, different effects can be obtained in the formation and conversion of tar. For gasification with air, which was the media used in this work, the parameter that influences the gasification products, including tar, is the equivalence ratio (ER) [1], and was calculated according to Eq. (1):

$$ER = \frac{Actual\ air}{Stoichiometric\ air} = \frac{m_{air}/m_{biomass}}{\left(m_{air}/m_{biomass}\right)stoichiometric} \qquad 1$$

Where Actual air is the actual air-to-fuel ratio, which is equal to the amount of air injected into the gasifier divided by the amount of biomass (used in gasification). Stoichiometric Air is the stoichiometric air-to-fuel ratio, which is equal to the amount of air needed to burn the biomass divided by the amount of biomass (used in combustion).

On the other hand, regarding moisture, the authors recommend that the moisture content of the biomass be as low as possible, and although this has little impact on the composition of the syngas and, consequently, on the lower heating value (LHV) of syngas when an external heat supply is available, if this is the most significant parameter in gasifier performance: the higher the humidity, the lower the cold gas efficiency (CGE). The CGE is a performance parameter, which is defined as the amount of energy contained in the clean gas with respect to the energy of the feed biomass, that is, it is the percentage of feed biomass energy still present clean syngas [12]. This occurs because feedstock with higher moisture content produce a smaller syngas flow rate, leading to a reduction in CGE [13]. In addition, that the moisture content affects the handling, storage and feeding of biomass. From the energy point of view, it is convenient to divide the biomass into two large groups, dry and wet biomass. It must be clarified that this classification is completely arbitrary, but it helps to better visualize the characterization of the conversion processes. This work considers the use of dry biomass, which is that which can be obtained naturally with an initial moisture content of less than 30%.

1.2.2. Gasifier types

Within the three main types of gasifiers in which gasification can be carried out, this work considers fixed bed (downdraft), bubbling bed and circulating fluidized bed (CFB) technologies.

Fixed bed gasification is the most common technology for the conversion of solid biomass. There are many types of fixed bed gasifiers with variable arrangements for both reactor design and reaction. The fixed bed gasifier can be classified according to the ways the gasifying agent enters the gasifier, that is, updraft, downdraft, crossdraft, and two-stage gasifier. The downdraft atmospheric gasifier is attractive for small-scale applications up to about 1.5 MWth [14]. Downdraft and updraft are two common types of fixed bed gasifier. Fluidized bed gasifiers are known for their reported advantages of feed flexibility and scalability, high heat and mass transfer rates, and high reaction rates.

1.3. Heating value

The Higher Heating Value (HHV) of the syngas in (MJ/Nm^3) can be calculated using Eq. (2).

$$HHV = ((CO\% * 3018 + H2\% * 3052 + CH4\% * 9500) * 0.01 * 4.1858) \qquad 2$$

The Lower Heating Value (LHV) is related to the ER, since with the increase in ER, the LHV decreases due to the decrease in H_2 and CO occurred in the oxidation reactions. Notwithstanding the foregoing, higher ER can improve syngas quality and also speed up coal/tar conversion According to some authors 3 MJ/Nm^3 is the minimum heating value necessary for the satisfactory operation of a gas engine, which means that the syngas obtained from biomass must satisfy this demand [3]. The lower heating value (LHV) of the syngas in MJ/Nm^3 can be obtained by Eq. (3) [15].

$$LHV = (0.126 * CO + 0.108 * H_2 + 0.358 * CH_4) \qquad 3$$

Where CO, H_2 and CH_4 are components of the syngas [4].

1.4. Tar formation

Both the yield and the concentration of tar in the product gas decreases with an increase in the ER. When ER values are high, large amounts of oxygen are present, which reacts with the volatiles in the flaming pyrolysis zone. Above an ER of 0.27, there is less tar formation, because almost all of the phenols are converted. This decrease is greater at higher temperatures. At a higher ER, the fraction of polynuclear aromatic hydrocarbon (PAH), benzene, naphthalene, and other 3- and 4-ring aromatics increases. While higher ER reduces the tar, it reduces the quality of the gas as well. The heating value of the gas is reduced because of nitrogen dilution from air [1].

2. Methodology

2.1. Simulations description

    i. All the simulations were carried out using the Aspen Plus simulation program.; the flow diagram appear in Fig. 1. The six main stages of the gasification model developed are:Biomass feeding,
    ii. Drying,
   iii. Pyrolysis,
   iv. Combustion at least 30%,
    v. Heterogeneous reactions, and
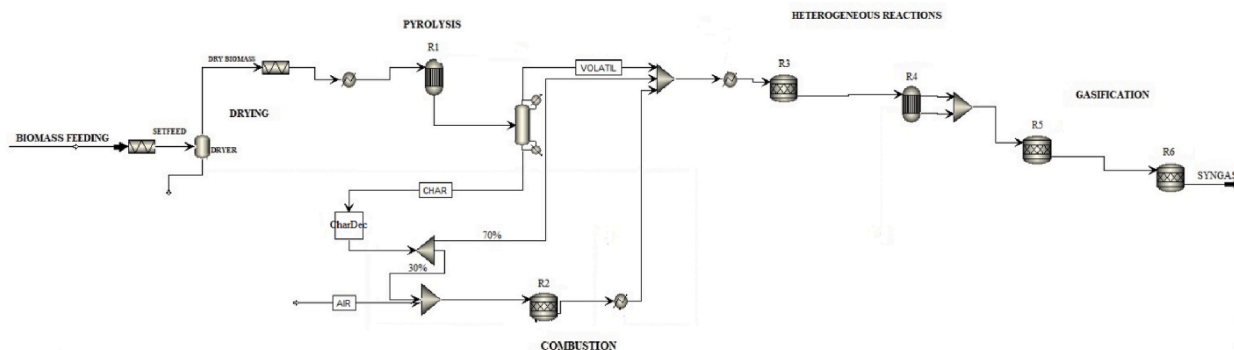   vi. Gasification

Fig. 1. Simulation flowsheet of the downdraft gasifier [9].

For the pyrolysis stage the reactor involved is a production reactor of the RYield type, this type of reactor is used when the chemical reactions that are carried out are unknown, but the data on the formation distribution of the reaction products, correlations, and/or empirical formulas where the formation of each of the products is determined, which is why a Fortran subroutine is used in this. For the Combustion step; The reactor involved is a Rstoic type stoichiometric reactor where the Char and Air currents are involved. This type of reactor has two main functions: simulation of combustion reactions and reactions where the fraction of conversion or production of one of the elements that participate in the reaction. For the step of Heterogeneous (secondary) reactions; The reactors involved are a Rstoic stoichiometric reactor, followed by a Requil equilibrium reactor, this second reactor uses Le Chatelier's principle of equilibrium in chemical reactions, where the reactions are of the following type: $aA + bB \leftarrow \rightarrow cC + dD$ where The variable to be modified is the temperature at which the reaction is carried out, so that depending on this variable, the reaction will be favored in one of the two directions. In the last step, Gasification; the transformation of the remaining coal into synthesis gas and the formation of methane from carbon monoxide and hydrogen are carried out. This process is carried out in two stages to facilitate its simulation, Rstoic stoichiometric reactors are used in both stages.

The reactors shown in Fig. 1 and the reactions involved in the simulation of the gasifier defined by stage are described in Table 1.

2.1.1. Assumptions and considerations

All simulations included the following considerations and assumptions: Biomass was specified as an unconventional solid by determining the standard enthalpy of formation and the physico-chemical composition of the feedstock. The HCOALGEN model was used to calculate biomass enthalpy and the DCOALIGT model was used to calculate biomass density, these models are used by various authors when the ultimate and proximate analysis are the basis, respectively [3]; The chosen thermodynamic model was Redlich-Kwong-Soave with Boston-Mathias modifications (RKS-BM). For the determination of the interaction parameters between pure components and the binary parameters, the model of non-random two-liquid electrolyte solutions (NRTL) is specified, this model is applied to calculate the phase equilibria by correlating the activity coefficients of a compound with their molar fractions in the corresponding liquid phase, in addition it has presented good results for the simulation with downdraft gasifiers of biomass gasification. For further information on how to properly select the property calculation method, see manual [16].

2.2. Feedstock data

In order to take advantage of any biomass through gasification, it is necessary to evaluate its capacity and ease of use. The chemical properties of the biomass, being a mixture of organic matter, can be determined from an ultimate analysis of the composition based on its content of Carbon, Hydrogen, Oxygen, Nitrogen and Sulfur (CHONS), and a proximate or thermos-gravimetric analysis to know the moisture content, fixed carbon and volatile material. Thus facilitating the calculation of material balance in the chemical reactions that take place during gasification. The biomass data used in this work are shown in Tables 2 and 3.

Biomasses covered for validation in this study for model validation are pine sawdust, bamboo dust, rice husk, and cane bagasse. The gasification of these biomass is a promising way to convert these residues into synthesis gas, mainly, and thus be able to use this syngas to generate heat, electricity and fuels. The simulation model is validated with the experimental results using six biomasses from the literature called pine sawdust (SD), bamboo dust (BD), rice husk (RH), sugarcane bagasse (SB), sawdust 2 (SD2) and rice husk 2 (RH2). The properties used for biomass validation were temperature, pressure, and inlet wet and dry flow rate, as well as moisture content before and after the dryer, proximate and ultimate analysis, and higher and lower heating value; for air as the gasification medium, the inlet temperature and pressure and the ER; and for the gasifier the technology used. The biomass properties and operating conditions

Table 1

Reactors and reactions involved in the simulation of biomass gasification.

Stage	Component	Reaction/Equation	Description
Biomass feeding	SETFEED	BDWOOD = RATE/24 * 2.20462 * 1000	Completely dry biomass rate
		WATFLO = XTARG * BDWOOD/(1 - XTARG)	Water in the feed, includes both free water and moisture in biomass
Drying	DRYER	$XH_2OIN = H_2OIN/(BDWOOD + H_2OIN)$	Water content in the feed
	DRYER	VF = (XH2OIN/(1-XH2OIN)- WLEVEL/(100-WLEVEL))/(XH2OIN/(1-XH2OIN))	Dryer Vapor Fraction
Pyrolysis	R1	$C_{component}*(m^3/kg_{biomass\ (dry)}*F_1) = a+bT + cT^2$	Fortran routine for calculating biomass decomposition into H_2, CH_4, N_2, H_2O, CO_2, CO C_2H_X, Tar and Char. F_1, Conversion factor to English units at 15 °C and 101.325 kPa.
	CharDec	$C_{component}*(kg_{char}/kg_{biomass}) = a+bT + cT^2$	USER module for the decomposition of char (solid part of the stream) into conventional elements H_2, CH_4, N_2, H_2O, CO_2, CO, C_2H_x and carbon
Combustion	R2	$C + O_2 \rightarrow CO_2$	With a conversion of 90% of the total carbon
	R2	$2C + O_2 \rightarrow 2CO$	With a conversion of 10% of the total carbon, partial combustion of Char
Heterogeneous reactions	R3	$2CO + O_2 \rightarrow 2CO_2$	Homogeneous oxidation reaction, CO oxidation
	R3	$2H_2 + O_2 \rightarrow 2H_2O$	Homogeneous oxidation reaction, gasification of H
	R4	$CO + H_2O \leftrightarrow CO_2 + H_2$	Homogeneous equilibrium reaction, water-gas shift reaction
	R4	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	Homogeneous equilibrium reaction, steam-methane reforming
Gasification	R5	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	Homogeneous oxidation reaction, methanation
	R6	$Carbón_{sólido} + CO_2 \leftrightarrow 2CO$	Heterogeneous equilibrium reaction, Bouduard
	R6	$Carbón_{Sólido} + H_2O \leftrightarrow CO + H_2$	Heterogeneous equilibrium reaction, water-gas reaction

Table 2
Biomass properties and operating conditions for model validation.

	Biomass type	Sawdust (SD)	Bamboo dust (BD)	Rice husk (RH)	Sawdust 2 (SD2)	Sugarcane bagasse (SB)	Rice husk 2 (RH2)
Biomass	Temperature (°C)	15.5	25	25	25	25	25
	Pressure (bar)	1	1	1	1	1	1
	Flow rate (kg/h)	40	18.8	18.8	18.8	20	20
	Wet Flow rate (ton/day)	0.96	0.451	0.451	0.451	0.48	0.48
	Dry Flow rate (ton/day)	0.672	0.410	0.412	0.409	0.459	0.432
	Initial Moisture (%)	30	9.12	8.7	9.43	4.4	9.95
	Final Moisture (%)	12	9.12	8.7	9.43	4.4	9.95
Air	Temperature (°C)	25	25	25	25	25	25
	Pressure (bar)	3	1	1	1	1	1
	ER	0.27	0.19, 0.24, 0.29, 0.35	0.19, 0.24, 0.29, 0.35	0.19, 0.24, 0.29, 0.35	0.1, 0.2, 0.25, 0.3, 0.35	0.1, 0.2, 0.25, 0.3, 0.35
Ultimate analysis (%)	Ash	0	2.62	19.6	1.1	2.94	0
	C	49.14	45.15	38.5	52.3	46.96	49.1
	H	6	4.8	4.79	5.17	5.72	3.78
	N	0.1	0.33	1.01	0.4	0.27	0.63
	Cl	0	0	0	0	0.02	0
	S	0	0	0	0	0.04	0.09
	O	44.76	47.1	36.1	41.7	44.05	46.4
Proximate analysis (%)	Moisture	30	9.12	8.7	9.43	10	9.95
	Fixed Carbon	15.4	14.7	12.01	15.63	18	11.55
	Volatile Matter	84.6	74.51	60.21	73.84	79.06	59
	Ash	0	1.68	19.6	1.1	2.94	19.5
Heating value (MJ/kg)	HHV	19.80	18.83	15.61	18.95	18.50	15.61
	LHV	17.10	14.74	13.72	18.14	16.10	15.10
Technology	Gasifier	Downdraft	Circulating fluidized bed	Bubbling fluidized bed			
	Reference	[9]	[17]	[17]	[17]	[18]	[18]

used for model validation are shown in Table 2.

2.2.1. Sargassum simulation

The biomass covered for the second step in this study for simulation is pelagic sargassum (Fig. 2). Massive beach arrivals of sargassum have created immediate problems in the Mexican southeast beaches for the fishing and tourism industries, leading to loss of revenue and unforeseen remediation costs. An example of this is the mortality between 30% and 50% of coral colonies from 2018 to date [23]. Taking this into consideration, this work focuses on evaluating the potential of a gasification process for this biomass to obtain syngas.

The results obtained in this study can be interpreted as trend lines for the performance of the sargassum gasification, this due to the lack of availability of experimental data of this raw material to be able to validate the simulations. However, sargassum gasification data can be used for subsequent simulations, given that the rice husk (RH) [17] presents the most similar compositions to sargassum with respect to the biomasses studied (Tables 2 and 3), especially regarding, C, H, N and ASH content and proximate analysis,. This practice has been used by some authors in simulations that aimed to study composition trends or certain biomass feedstock and whose experimental gasification results were not available [2].

The properties of the biomasses used to carry out the sargassum gasification simulations were obtained from 4 bibliographic sources [19–22] and one from an own experiment (S5), the latter was carried out an elemental analysis using a PerkinElmer elemental analyzer model PE2400. The properties were the ultimate and proximal analysis and heating value of the biomass, as well as the place of collection of the sample. These are shown in Table 3.

3. Results

The experimental results [9,17,18] were considered for the validation of the present model with the operating conditions used that are shown in Table 2. Afterwards, a simulation of the sargassum gasification was carried out with the data from Refs. [19–22] and tests carried out in an elemental analysis laboratory of our university, which are shown in Table 3, with the gasification conditions of the Duran reference model [9].

3.1. Simulation model validation

The performance of the simulation process was evaluated based on the comparison of the percentage molar composition and the heating value of the obtained syngas. This comparative analysis between the simulated results in Aspen Plus and the experimental ones

Table 3

Sargassum properties and operating conditions for simulation.

	Biomass type	Sargassum natans (S1)	Sargassum muticum (S2)	Sargassum muticum (S3)	Sargassum (S4)	Sargassum fluitans and natans (S5)	Sargassum natans (S6)
Biomass	Temperature (°C)	25	25	25	25	25	25
	Pressure (bar)	1	1	1	1	1	1
	Flow rate (kg/h)	20	20	20	20	20	20
	Wet Flow rate (ton/day)	0.48	0.48	0.48	0.48	0.48	0.48
	Dry Flow rate (ton/day)	0.336	0.336	0.336	0.4608	0.455	0.336
	Initial Moisture (%)	30	30	30	4	5.3	30
	Final Moisture (%)	10.46	10.46	10.46	4	5.3	10.46
Air	Temperature (°C)	25	25	25	25	25	25
	Pressure (bar)	3	3	3	3	3	3
	ER	0.3, 0.35	0.22, 0.25, 0.3, 0.35	0.22, 0.25, 0.3, 0.35	0.21, 0.25, 0.3, 0.35	0.21, 0.25, 0.3, 0.35	0.18, 0.2, 0.25, 0.3, 0.35
Ultimate analysis (%)	C	28.9	30.1	30.7	34.1	24	25.9
	H	6.2	4.2	4	3.9	3.7	5.57
	N	4	3.6	4.9	1.3	1.1	3.58
	Cl	0	0	0	0	0	0
	S	1.4	0.8	1.5	0	1	1.22
	O	27	28.1	29.6	45.2[a]	37.7	24.18
Proximate analysis (%)	Moisture	7.05			4	5.3	10.13
	Fixed Carbon	11.6			19.2	11.9	11.6
	Volatile Matter	48.85			61.3	50.3	48.85
	Ash	32.5	33.2	29.3	15.5	32.5	29.09
Heating value (MJ/kg)	HHV	12.20	12.05	16.37		10.10	
	LHV	9.70				9.50	8.68
	Location	Zhanjiang of Guangdong province, China	Walpole Bay, Margate, England (summer)	Walpole Bay, Margate, England (spring)	Whitecap Beach, Corpus Christi, Texas, USA	Puerto Morelos, Quintana Roo, México	Zhanjiang of Guangdong province, China
	Reference	[19]	[20]	[20]	[21]	Own data	[22]

[a] Calculated by difference.
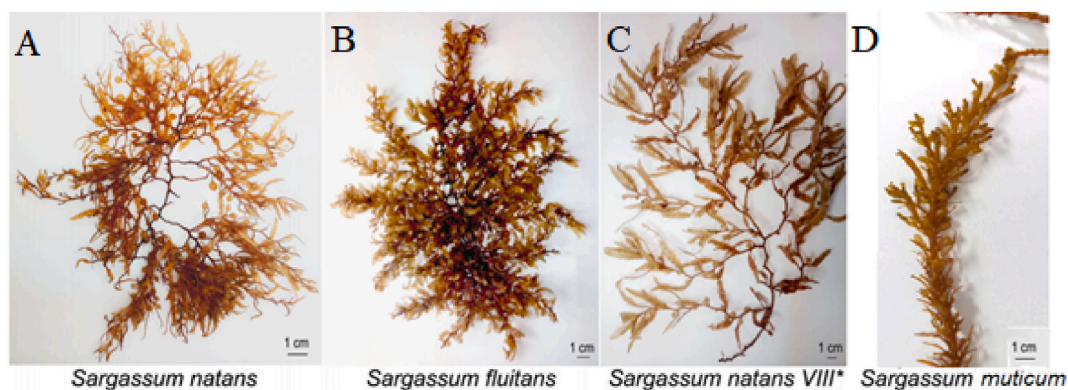
Fig. 2. The biomasses covered in this study are sargassum natans (A, C), fluitans (B) and muticum (D). ([10] with own modifications).

on the variation of the percentage molar composition of the syngas, as well as the error due to difference, are shown in Tables 4–9.

For the validation simulation (Tables 6–9) data were obtained with an ER of 0.29 and 0.35, where the smallest error due to difference is obtained when the ER is 0.35, and this can be observed in the values of hydrogen and methane, and in the experiments where the gasification technology is circulating fluidized bed. (Tables 5–7).

When the ER is 0.35, those that obtain the smallest error are RH and BD, for H_2 with 0.3 and 0.32, for CO 0.6 and 1.36 respectively; and for CH_4, RH with 0.1 and SD2 with 0.9. On the other hand, a smaller difference is observed for the error CO_2 when the ER is 0.29 for

Table 4

Base validation SD.

Gas Composition (mole %)	% experimental[a]	% simulation
H_2	12	9.2
CO	20	19.6
N_2	52	57.7
CO_2	11	10.4
CH_4	5	3
Total	100	100

[a] [9].

Table 5

Validation BD.

Gas Composition (mole %)	% experimental	% simulation	Error (by diff)	% experimental	% simulation	Error (by diff)
ER	0.29			0.35		
H_2	6.9	8.1	1.2	6.8	7.1	0.3
CO	17.2	20.3	3.1	16.4	17.7	1.3
CO_2	11.8	7.3	4.5	12.5	6.3	6.1
CH_4	4.4	2.17	2.23	4.3	1.9	2.4

Table 6

Validation SD2.

Gas Composition (mole %)	% experimental	% simulation	Error (by diff)	% experimental	% simulation	Error (by diff)
ER	0.29			0.35		
H_2	9.0	10.2	1.2	8.5	9.4	0.9
CO	15.2	22.4	7.2	14.8	20.7	5.9
CO_2	12.8	7.5	5.3	12.7	7.0	5.7
CH_4	3.0	2.0	1.0	2.7	1.8	0.9

Table 7

Validation RH.

Gas Composition (mole %)	% experimental	% simulation	Error (by diff)	% experimental	% simulation	Error (by diff)
ER	0.29			0.35		
H_2	6.8	8.1	1.3	6.7	7.0	0.3
CO	16.3	17.7	1.4	14.8	15.4	0.6
CO_2	14.3	6.8	7.5	13.4	5.9	7.5
CH_4	2.5	2.0	0.5	1.8	1.7	0.1

Table 8

Validation RH2.

Gas Composition (mole %)	% experimental	% simulation	Error (by diff)	% experimental	% simulation	Error (by diff)
ER	0.25			0.35		
H_2	8.0	12.7	4.7	6.5	10.6	4.1
CO	13.0	27.6	14.6	10.0	22.9	12.9
N_2	30.0	41.1	11.1	37.0	47.7	10.7
CO_2	17.3	8.4	8.9	17.0	7.0	10.0
CH_4	7.5	2.0	5.5	5.5	1.7	3.8

Table 9

Validation SB.

Gas Composition (mole %)	% experimental	% simulation	Error (by diff)
ER	0.35		
H_2	6.0	8.7	2.7
CO	15.0	20.5	5.5
N_2	45.0	49.4	4.4
CO_2	17.0	7.5	9.5
CH_4	4.0	2.2	1.8

BD with 4.5 and SD2 with 5.3. Being the RH the one with the best approximation in a general way in the composition.

For the comparison of the experimental and simulation higher heating value, Eq. (2) was used and the results are shown in Table 10, where it is observed in the same way that the lowest percentage error is found in the RH syngas for the ER of 0.29 and 0.35 followed by the SB, with percentage errors of 5.2, 4.33 and 6.68 respectively.

3.2. Sargassum gasification simulation

The simulation of sargassum gasification as study biomass was carried out with the information on the properties of the biomasses and the operating conditions shown in Table 3. The result of the percentage molar composition of the syngas obtained is shown graphically on Figs. 3 and 4.

Fig. 3 show the molar composition of the synthesis gas obtained from the gasification of sargassum as biomass with ER of 0.2, 0.25, 0.3 and 0.35. An approximate average of the six sargassum has a percentage molar composition for hydrogen of 8% (Fig. 3, A), for nitrogen 45% (Fig. 3, E), for carbon monoxide 20% (Fig. 3, B), for carbon dioxide 7% (Fig. 3, C), for methane 3% (Fig. 3, D), for 0.4% argon, 17% for water (Fig. 3, F), and 2% for oxygen, this being the one with a greater slope when varying the ER.

It is also observed that the tars generated in the synthesis gas decrease with increasing ER, $C_{10}H_8$ (Fig. 4, A) and C_6H_6 (Fig. 4, B).

For the heating value of the gas product of the first simulation with sargassum as raw material, Eq. (2) and Eq. (3) were used, and the results of the heating value of the resulting gas are shown in Table 11 and Fig. 5, where the lower and higher heating value of sargassum for ER 0.3 is shown in Fig. 5, A and for ER 0.35 in Fig. 5, B. It is observed that the highest heating value was obtained with an ER of 0.3, this is shown in S4 and S5, which obtained an LHV of 4.8 MJ/Nm^3 and 4.2 MJ/Nm^3, respectively. The average value obtained for the heating value is 4 MJ/Nm^3, which means that the synthesis gas obtained is suitable for use for gas engines that consume fuel gases with medium-high heating value [4], this using the selected biomass and under certain conditions of operation (T = 600 °C and ER = 0.3).

A second simulation was carried out using sargassum S2, S3, S4 and S5 as study biomasses, varying the input biomass flow from 10 to 50 kg/h, in ranges of 10 kg/h, but maintaining an ER of 0.3 and 0.35 and the results are shown in Tables 12–15. Where it is observed that the percentage molar composition is constant regardless of the input biomass flow.

4. Discussion and conclusions

The results of the first part of the simulation indicated that the simulation model can be used as an approximation for the gasification of different biomasses and with different gasification technologies (downdraft, circulating fluidized bed and bubbling fluidized bed) taking into account that with the downdraft and circulating fluidized bed gasification technologies, results closer to the experimental ones are obtained. The performance of the process was evaluated based on the experimental and simulation comparison of the percentage molar composition and the heating value of the syngas obtained, where the best approximation found was for the validation of RH (circulating fluidized bed) with an error in the higher heating value of 5.20 and 4.33 for the ER of 0.29 and 0.35, respectively. The biggest difference error was obtained with the RH2 validation, with 36.49% for 0.25 ER and 19.01 for 0.35 ER in the HHV comparison. This may be due to the fact that the ASH content of its ultimate and proximate analysis are different, since this value was neglected in the ultimate analysis by the author of the reference. The smallest variations between the simulation model used and the literature data may be due to the fact that the simulation model considers the combustion of 30% of the biomass and therefore an energy balance.

The simulation model used in this study is capable of estimate the composition of the syngas obtained through the gasification of sargassum. Where the syngas conditions that were studied were their percentage molar composition of H_2, CO, CO_2 and CH_4, as well as their HHV and LHV.

Although there is a lack of experimental data on the gasification of this raw material (sargassum) to be able to validate the simulations with the conditions chosen in this study; the results of the validation simulation agree with the data from the literature, indicating that the results obtained for the second step of this study can be interpreted as trend lines for the performance of sargassum gasification.

The results of the simulation of sargassum gasification was carried out with information on the properties of the biomass from five bibliographical references, a synthesis gas was obtained with a percentage molar composition that follows a trend line with the exception from S1 (which was not simulated) with ER less than 0.3, in addition, syngas was obtained with a LHV that varies between 2.6 and 4.8 MJ/Nm^3 for ER of 0.3 and 0.35, where the highest heating value corresponds to S4 and S5 with 4.8 MJ/Nm3 and 4.2 MJ/Nm^3 respectively, both with an ER of 0.3.

On the other hand, with the increase of the ER, the reduction of the heating value of the syngas is also observed and therefore of its

Table 10
HHV of the resulting syngas.

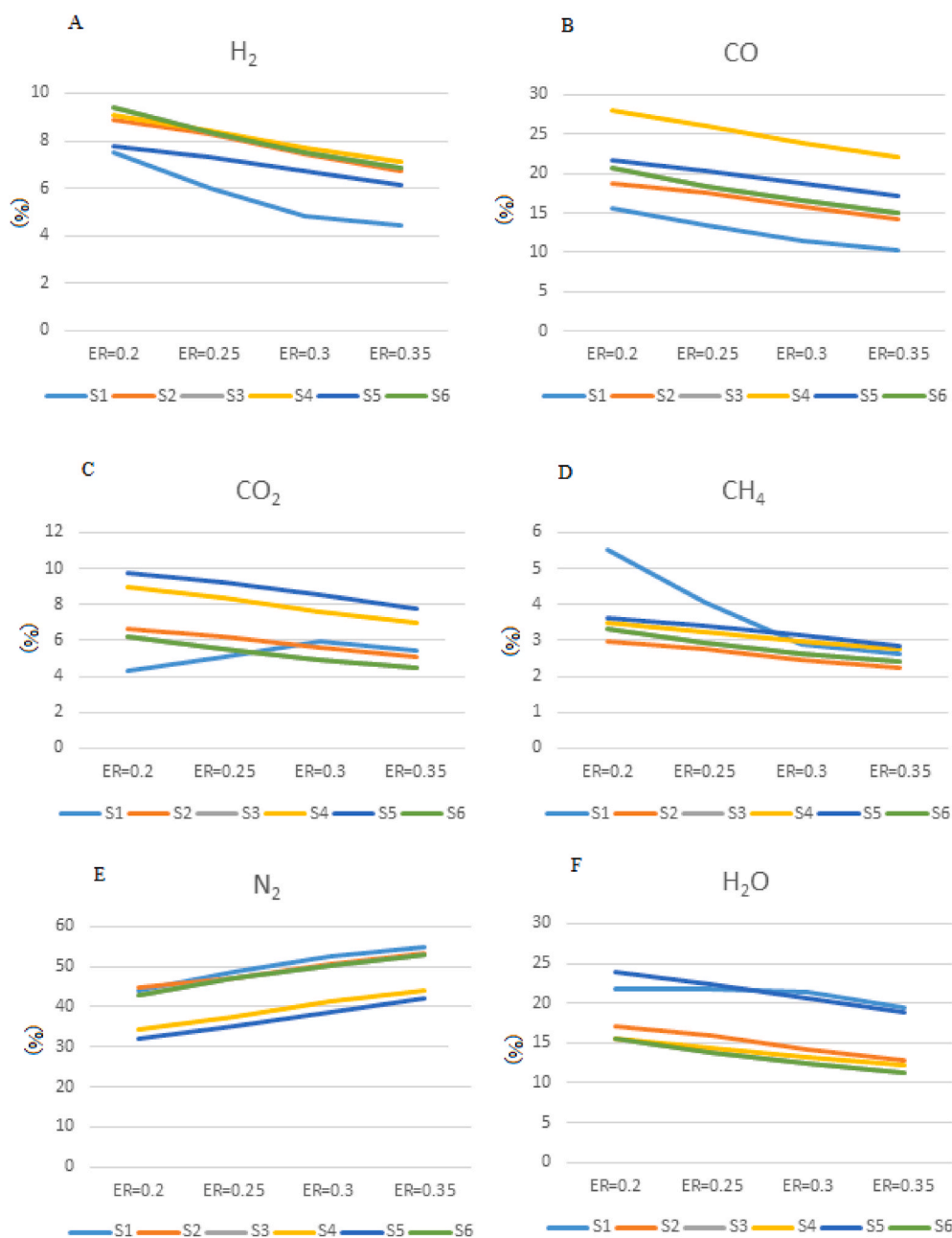| Biomass	BD		SD		RH		RH2		SB
ER	0.29	0.35	0.29	0.35	0.29	0.35	0.25	0.35	0.35
HHV exp (MJ/Nm^3)	4.804	4.650	4.263	4.029	3.922	3.441	5.646	4.280	4.252
HHV sim (MJ/Nm^3)	4.516	3.951	4.961	4.579	4.137	3.597	4.137	3.597	4.556
Error (%)	6.37	17.70	14.07	12.01	5.20	4.33	36.49	19.01	6.68

Fig. 3. molar composition of (A) hydrogen, (B) carbon monoxide, (C) carbon dioxide, (D) methane, (E) nitrogen and (F) water.

quality (Table 11), where the sargassum with the highest lower heating value decreases, being the case of S4 and S5, for these two sargassum, it was observed that with the increase in ER from 0.3 to 0.35, the LHV decreases due to the decrease in H_2 and CO in the oxidation reactions, for S4 from 4.8 MJ/Nm^3 to 4.5 MJ/Nm^3 and for S5 from 4.1 MJ/Nm^3 to 3.8 MJ/Nm^3. It is also observed that they fall within the gasification range of conventional biomes of 4.5–5.0 MJ/Nm^3 for downdraft and 4–7 MJ/Nm^3 with air as the gasification medium. Another important observation is that S4 and S5, which have a HHV for ER of 0.3, 5.3 MJ/Nm^3 and 4.5 MJ/Nm^3, respectively, have a value very close to pine sawdust (Table 10), a biomass very commonly used for gasification, which could prove than the quality of the synthesis gas obtained from this type of biomass. The values are similar to those obtained in the gasification of terrestrial biomass (Table 10) and the one obtained by some authors for legume straw [3], in addition to the fact that the minimum heating value necessary for the satisfactory operation of a gas engine is approximately 3 MJ/Nm^3, and the syngas obtained from the used biomasses, with the exception of S1, are greater than this value.

Tar is one of the byproducts of insufficient biomass conversion [24]. Within the estimation of the tars (light aromatics) generated in the syngas, it is observed that these decrease with the increase in ER (Fig. 4), with the highest values of molar composition of
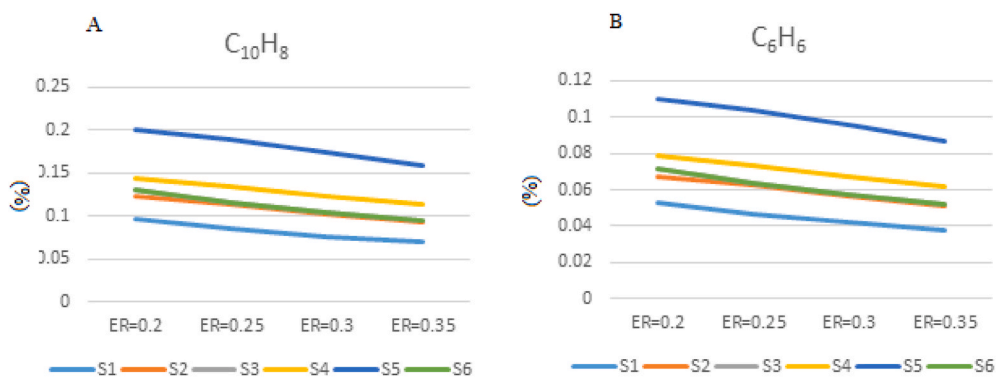
Fig. 4. molar composition of tar: (A) naphthalene and (B) benzene.

Table 11
Heating value of the resulting syngas.

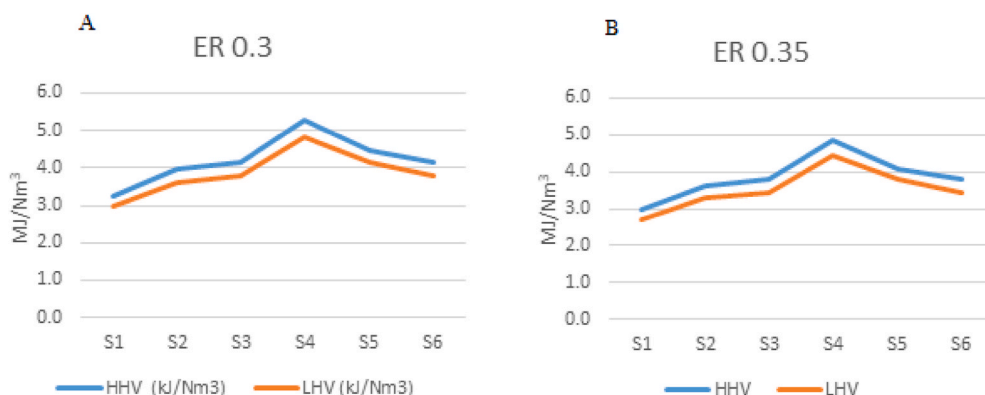| Biomass	S1		S2		S3		S4		S5		S6	
ER	0.3	0.35	0.3	0.35	0.3	0.35	0.3	0.35	0.3	0.35	0.3	0.35
HHV (MJ/Nm^3)	3.257	2.965	3.983	3.607	4.165	3.782	5.266	4.853	4.485	4.081	4.165	3.782
LHV (MJ/Nm^3)	2.961	2.696	3.623	3.280	3.792	3.443	4.840	4.461	4.165	3.790	3.792	3.443

Fig. 5. Lower and higher heating value of sargassum for (A) ER 0.3 and (B) ER 0.35.

Table 12
molar composition of the synthesis gas with an ER 0.3 and 0.35 varying the input biomass flow for S2.

Biomass flow (kg/h)	10	20	30	40	50	10	20	30	40	50
ER	0.3					0.35				
H$_2$ (mole %)	7.42	7.43	7.42	7.42	7.42	6.73	6.73	6.73	6.73	6.73
CO (mole %)	15.72	15.74	15.72	15.72	15.72	14.26	14.25	14.26	14.26	14.26
CO$_2$ (mole %)	5.57	5.58	5.57	5.57	5.57	5.05	5.05	5.05	5.05	5.05
CH$_4$ (mole %)	2.47	2.47	2.47	2.47	2.47	2.24	2.24	2.24	2.24	2.24

Table 13
molar composition of the synthesis gas with an ER 0.3 and 0.35 varying the input biomass flow for S3.

Biomass flow (kg/h)	10	20	30	40	50	10	20	30	40	50
ER	0.3					0.35				
H$_2$ (mole %)	7.49	7.53	7.53	7.53	7.53	6.84	6.84	6.84	6.84	6.84
CO (mole %)	16.42	16.52	16.52	16.52	16.52	15.01	15.00	15.01	15.01	15.01
CO$_2$ (mole %)	4.93	4.96	4.96	4.96	4.96	4.50	4.50	4.50	4.50	4.50
CH$_4$ (mole %)	2.63	2.64	2.64	2.64	2.64	2.40	2.40	2.40	2.40	2.40

Table 14
molar composition of the synthesis gas with an ER 0.3 and 0.35 varying the input biomass flow for S4.

Biomass flow (kg/h)	10	20	30	40	50	10	20	30	40	50
ER	0.3					0.35				
H_2 (mole %)	7.73	7.73	7.73	7.73	7.73	7.13	7.12	7.13	7.13	7.13
CO (mole %)	23.90	23.89	23.90	23.90	23.90	22.05	22.02	22.05	22.05	22.05
CO_2 (mole %)	7.63	7.63	7.63	7.63	7.63	7.04	7.03	7.04	7.04	7.04
CH_4 (mole %)	2.98	2.98	2.98	2.98	2.98	2.75	2.75	2.75	2.75	2.75

Table 15
molar composition of the synthesis gas with an ER 0.3 and 0.35 varying the input biomass flow for S5.

Biomass flow (kg/h)	10	20	30	40	50	10	20	30	40	50
ER	0.3					0.35				
H_2 (mole %)	6.62	6.62	6.62	6.62	6.65	6.13	6.13	6.13	6.13	6.16
CO (mole %)	18.49	18.49	18.49	18.49	18.49	17.13	17.11	17.12	17.12	17.12
CO_2 (mole %)	8.36	8.36	8.36	8.36	8.36	7.74	7.73	7.74	7.74	7.74
CH_4 (mole %)	3.09	3.09	3.09	3.09	3.08	2.86	2.86	2.86	2.86	2.85

naphthalene being found by S5; going from 0.2% to 0.16% for ER of 0.2 and 0.35 respectively, the lowest values were obtained for S1 going from 0.1% to 0.07%. In the case of the percentage molar composition of benzene, the highest values are also observed in S5 with 0.11% for ER of 0.2, and 0.09% for ER of 0.35; in S1 the lowest values are observed again with 0.05% and 0.04% for the ER of 0.2 and 0.35 respectively. This is because a higher ER allows more oxygen to react with the volatiles in the pyrolysis zone [1], the quality of the gas is also reduced with high ER rates because the heating value of the gas is reduced due to the dilution of nitrogen from the air used (Table 10). The high variability in the concentrations of the respective light aromatic tars can be attributed to the volatile nature of the compounds [25].

Tar amount and its composition are influenced by the gasification technology, operating conditions and the biomass used as feedstock [26]. Taking S5 as a reference, the mass density of the light tars (benzene and naphthalene) it is observed that for an ER of 0.21 a density of 1.09 g/Nm^3 was obtained, for the ER of 0.25 a density of 1.035 g/Nm^3, for the ER of 0.3 a density of 0.96 g/Nm^3 and for the ER of 0.35 a density of 0.88 g/Nm^3. Taking reference [27] into consideration, S5 has a 10 times higher density compared to cedar granules with 0.084 g/Nm^3 for naphthalene and 0.011 g/Nm^3 for benzene. The tar concentration obtained is higher than those required for synthesis (<0.001 g/Nm^3) or heat and power applications (<0.001–0.1 g/Nm^3) [26]. Therefore, a more extensive study of the tar content should be carried out in addition to seeking a tar removal strategy for this biomass gasification.

Lastly, for the second step of the simulation, using sargassum S2, S3, S4 and S5 as study biomasses, varying the inlet biomass flow from 10 to 50 kg/h, in ranges of 10 kg/h, it is observed that the percentage molar composition is constant for a constant ER. So we can assume that this input mass flow does not have any effect on the percentage molar composition of the syngas obtained in the gasification.

In recent years, emphasis has been placed on the importance of using biomass as a potential bioenergy resource; In the case of sargassum in the Mexican Caribbean, only bioenergetics valorization studies have been carried out [28]. With the HHV data obtained from this work, it is possible to interpret the bioenergetic potential of sargassum to be used and contribute to the optimization and use of this residue as a resource to generate value, in addition to reducing the primary problems generated by it. This study is particularly useful to have a preliminary result of the quality of the synthesis gas obtained from gasification and the feasibility of its use to satisfy the growing demand for access to modern energy sources.

Author contribution statement

Amalinalli Velázquez Hernández: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Javier E. Aguillón Martínez: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Data availability statement

Data included in article/supp. material/referenced in article.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] Prabir Basu, Biomass Gasification and Pyrolysis Practical Design and Theory", Elsevier Inc. All rights reserved, 2010.

[2] Ingrid Lopes Motta, Nahieh Toscano Miranda, Rubens Maciel Filho, Maria Regina Wolf Maciel. (2019) "Sugarcane bagasse gasification: simulation and analysis of different operating parameters, fluidizing media, and gasifier types". Elsevier, Biomass and Bioenergy 122 (2019) 433–445.

[3] Y. Cao, Q. Wang, J. Du, J. Chen, Oxygen-enriched air gasification of biomass materials for high-quality syngas production, 2019, El sevier, Energy Conversion and Management 199 (2019), 111628 (China).

[4] Deepak Kumar Singh, Jeewan V. Tirkey, "Modeling and multi-objective optimization of variable air gasification performance parameters using Syzygium cumini biomass by integrating ASPEN Plus with Response surface methodology (RSM)" Elsevier, Int. J. Hydrogen Energy 46 (2021) (2021) 18816–18831.

[5] Liang Zhou, Zhiyong Yang, Anjiang Tang, Hongsheng Huang, Deju Wei, Erlei Yu, Wei Lu, Steam-gasification of biomass with CaO as catalyst for hydrogen-rich syngas production, 2019, Elsevier J. Energy Inst. 92 (2019) 1641–1646 (China).

[6] Mahdi Faraji, Majid Saidi, "Hydrogen-rich syngas production via integrated configuration of pyrolysis and air gasification processes of various algal biomass: process simulation and evaluation using Aspen Plus software". Elsevier, Int. J. Hydrogen Energy 46 (2021) (2021) 18844–18856.

[7] S. Rupesh, C. Muraleedharan, P. Arun, ASPEN plus modelling of air–steam gasification of biomass with sorbent enabled CO2 capture 2016 El sevier, Resource-Efficient Technologies 2 (2016) 94–103.

[8] J. He, K. Goransson, U. Soderlind, W. Zhang, "Simulation of biomass gasification in a dual fluidized bed gasifier" Biomass Conv, 2012, Bioref 2 (2012) 1–10, https://doi.org/10.1007/s13399-011-0030-2.

[9] R. Durán, J. Efrén, M. Aguillón, E. Javier, Simulación en aspen plus® de la generación de alquitranes obtenidos en la gasificación de biomasa", memorias del XIX congreso internacional anual de la SOMIM, 2013, pp. 1404–1411, 978-607-95309-9-0.

[10] Cinvestav, Sargazo, Conociendo Al Enemigo", Revista: Avance Y Perspectiva, Volumen, vol. 5, 2019. Numero 3.

[11] FAO, La seguridad en el mar como parte integrante de la ordenación pesquera, Circular de pesca N°966, 2017. ISSN 1020-1467.

[12] J.C. González-Rocha, G. Urquiza-Beltrán, R. y Longoria-Ramírez, Estudio paramétrico de la gasificación del coque de petróleo mexicano: efecto de la alimentación de coque de petróleo sobre las características energéticas del gas sintético (gassin), Scielo, Ingeniería, investigación y tecnología 12 (2011) 3. Versión On-line ISSN 2594-0732, versión impresa ISSN 1405-7743.

[13] Ingrid Lopes Motta, Nahieh Toscano Miranda, Rubens Maciel Filho, Maria Regina Wolf Maciel, Biomass gasification in fluidized beds: a review of biomass moisture content and operating pressure effects, 2018, Elsevier Renew. Sustain. Ener. Rev. 94 (2018) 998–1023.

[14] P.P. Dutta, V. Pandey, A.R. Das, S. Sen, D.C. Baruah, Down draft gasification modelling and experimentation of some indigenous biomass for thermal applications, 2014, El sevier, Energy Procedia 54 (2014) 21–34.

[15] Mohamad Syazarudin Md Said, Wan Azlina Wan Abdul Karim Ghani, Tan Hong Boon, Siti Aslina Hussain, Denny Kok Sum Ng, Thermochemical conversion of napier grass for production of renewable syngas, 2019, Processes 7 (2019) 705, https://doi.org/10.3390/pr7100705.

[16] A.P. Manual, Physical Property Systems, Physical Property Methods and Models 11, vol. 1, Aspen Technology Inc, 2001.

[17] Debarshi Mallick, Pinakeswar Mahanta, S. Vijayanand, Moholkar, "Co-gasification of biomass blends: performance evaluation in circulating fluidized bed gasifier, 2020, Energy 192 (2020), 116682. Elsevier.

[18] P. Manikandan, V. Christus Jeya Singh, Prediction of gas composition of a fluidized bed gasifier in a sugarcane bagasse- modeling, 2020, in: IWCASME 2020, IOP Conf. Series: Materials Science and Engineering, vol. 983IOP Publishing, 2020, 012013, https://doi.org/10.1088/1757-899X/983/1/012013.

[19] John J. Milledge, Patricia J. Harvey, Golden tides: problem or golden opportunity? The valorisation of sargassum from beach inundations, 2016, J. Mar. Sci. Eng. 4 (2016) 60, https://doi.org/10.3390/jmse4030060.

[20] John J. Milledge, Patricia J. Harvey, Ensilage and anaerobic digestion of Sargassum muticum, 2016, J. Appl. Phycol. 28 (2016) 3021–3030, https://doi.org/10.1007/s10811-016-0804-9.

[21] Ketwalee Kositkanawuth, Melanie L. Sattler, Brian H. Dennis, Investigation of Co-pyrolysis between Sargassum Seaweed and Polystyrene Pellets, 2012. Extended Abstract 2012-A-324-AWMA Corpus ID: 99756046.

[22] Shuang Wang, Wang Qian, Xiumin Jiang, Xiangxin Han, Hengsong Ji, Compositional analysis of bio-oil derived from pyrolysis of seaweed, 2013, Elsevier Energy Conver. Manag. 68 (2013) 273–280.

[23] Marta García-Sánchez, Caroline Graham, Elisa Vera, Edgar Escalante-Mancera, Lorenzo Álvarez-Filipa, I. Brigitta, van Tussenbroek, "Temporal changes in the composition and biomass of beached pelagic Sargassum species in the Mexican Caribbean". Elsevier, 2020, Aquatic Botany 167 (2020), 103275.

[24] Tayachew Nega, , Nigus Gabbiye Habtu, AssefaTesfaye, , Getahun Tassew Melesse, Ermias Aswossie, 2022, Biomass Energy Conversion in a Gasifier for Injera Baking Mitad Application" Heliyon, vol. 8, 2022, e12128.

[25] E. Menya, J. Olwa, P. Hagstromb, M. Okure, Assessment of pollution levels resulting from biomass gasification, 2014, Elsevier. Journal of Environmental Chemical Engineering 2 (2014) 1228–1235.

[26] M. Cortazar, L. Santamaria, G. Lopez, J. Alvarez, L. Zhang, R. Wang d, X. Bi, M. Olazar, A comprehensive review of primary strategies for tar removal in biomass gasification, 2023, El sevier. Energy Conversion and Management 276 (2023), 116496.

[27] Anh Vo Cong, Hiroshi Enomoto, Rizqi Fitri Naryanto, Kazushi Fukadu, Zong Zheng, Chunti Chuntima, Reiji Noda, Gasification tar compounds, Bioresources 15 (1) (2020) 1773–1790.

[28] A. Sosa O. José, R. José, C. Laines, Z. David Guerrero, D. Anabel González, A. Donato, J. Figueiras, K. Heidi, G. Osorio, L. Berenice Evia, Bioenergetic valorization of Sargassum fluitans in the Mexican Caribbean: the determination of the calorific value and washing mechanism, AIMS Energy 10 (1) (2022) 45–63, https://doi.org/10.3934/energy.2022003.