Kinetic study of supercritical water gasification of cellulose from Biomass

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Abstract. This work carried out the supercritical gasification of cellulose in water (SCWG). The products obtained from the reaction were measured and their kinetic parameters were determined. The SCWG of cellulose was carried out in a supercritical PFR reactor evaluating three reaction temperatures: 372 °C, 374 °C, 376 °C for a reaction time of 15 min. The reaction products were analyzed by gravimetry, liquid chromatography HPLC and gas chromatography. The kinetic parameters of the SCWG reaction were then determined. This reaction produces hydrogen, with high energy potential, and lactic acid, a high-value product. The results show that, by raising the temperature of cellulose from subcritical to supercritical, the production of both compounds increases, reaching its highest concentration at a temperature of 376 °C and pressure of 3300 psi. To determine the kinetic parameters, integrated equations were used, revealing that the SCWG reaction follows first-order kinetics under the analyzed operating conditions. and its kinetic constants for each temperature are: $k_1 = 0.01386 \ [min]^{-1}$, $k_2 = 0.01538 \ [min]^{-1}$ and $k_3 = 0.01529 \ [min]^{-1}$. This study advances the understanding of supercritical gasification as an alternative to convert waste into valuable products.

Keywords: Biomass, Cellulose, SCWG, Kinetic, Reaction Order.

Resumen. Este trabajo realizó la gasificación de celulosa en agua a temperatura supercrítica (SCWG). Se midieron los productos obtenidos de la reacción y se determinaron sus parámetros cinéticos. La SCWG de celulosa se llevó a cabo en un reactor PFR supercrítico evaluando tres temperaturas de reacción: 372 °C, 374 °C, 376 °C para un tiempo de reacción de 15 min. Mediante gravimetría, cromatografía de líquidos HPLC y cromatografía de gases se analizaron los productos de reacción. Posteriormente se determinó los parámetros cinéticos de la reacción de SCWG. Esta reacción produce hidrógeno, con alto potencial energético, y ácido láctico, un producto de alto valor. Los resultados muestran que, al elevar la temperatura de la celulosa de subcrítica a supercrítica, aumenta la producción de ambos compuestos, llegando a su mayor concentración a una temperatura de 376 °C y presión de 3300 psi. Para determinar los parámetros cinéticos, se usaron ecuaciones integradas, revelando que la reacción de SCWG sigue una cinética de primer orden bajo las condiciones de operación analizadas. y sus constantes cinéticas para cada temperatura son: $k_1 = 0.01386 \ min^{-1}$, $k_2 = 0.01538 \ min^{-1}$ y $k_3 = 0.01529 \ min^{-1}$. Este estudio avanza en la comprensión de la gasificación supercrítica como alternativa para convertir residuos en productos valiosos.

Palabras claves: Biomasa, Celulosa, SCWG, Cinética, Orden de reacción.

1. INTRODUCTION

Environmental pollution caused by fossil fuels, in addition to the increase in their costs, has made it essential to search for new technologies that contribute to the generation of clean energy. It is estimated that by 2040 around 45.5 billion metric tons of CO2 will be emitted into the atmosphere. (Mondragón 2021)

Biomass emerges as one of the potential alternatives to modify dependence on fossil fuels, being the fourth most abundant energy resource after coal, oil and natural gas. (Shah and Venkatramanan 2019).

Gasification appears as one of the most favorable options for the processing of lignocellulosic biomass since its products can serve all types of energy markets that involve generation of heat, electricity and transportation fuels (Yakaboylu et al. 2015); In addition, its main product known as synthesis gas, has a high hydrogen content, being an option for the production of hydrogen from renewable sources.

In agricultural countries like Ecuador, the generation of agro-industrial waste represents an opportunity to obtain products with high added value. (Kaza et al. 2018) Permanent crops can be found such as: cocoa, plantain, sugar cane, banana and transitory crops such as corn and rice. In 2014, the production of agricultural waste exceeded 10 million tons. This large amount of waste shows the need to use it through its conversion to energy, heat, and biofuels, generating products with high added value. (Serrano et al. 2017)

For the use of waste such as cellulose, it is of vital importance to develop the kinetics and mechanism of the SCWG reaction with the purpose of optimizing the production of synthesis gas and consequently laying the foundations for a future scaling of the process (Li et al. 2022). By using the integrated kinetic equations and the Arrhenius equation, the aim is to find a linear relationship between the kinetic constant and the temperature that allows determining the kinetic parameters of the reaction from the experimental data obtained in the SCWG process.

1.1. Gasification in water at supercritical temperature (SCWG)

Álvarez Alonso (2021) Supercritical water gasification (SCWG) uses thermal technology to transform biomass waste into hydrogen-rich syngas at high temperatures and pressures. The supercritical state exists at pressure and temperature above the critical point of water (22.1 MPa, 374 °C), where water has no distinction between liquid and gas phase. In the SCWG we have the dissolution properties of liquids and the diffusion properties of gases. During the supercritical state of water there is no surface tension as there are no liquid or gas phase boundaries as the two phases coexist. Water above its critical pressure improves mass transfer and solvation properties, in addition to having high diffusivity as a gas and the viscosity of a liquid. (Okolie 2021).
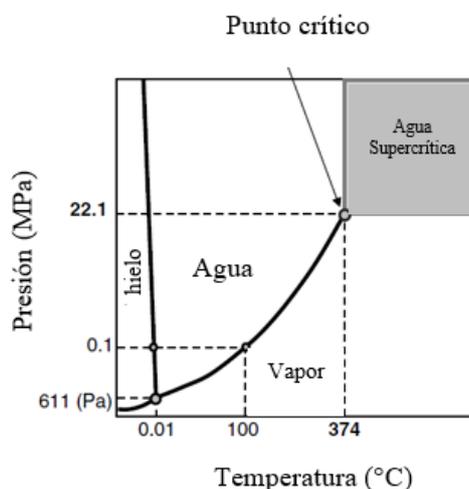

Figure 1. Phase diagram for supercritical water. (Basu 2010)

If the biomass contains high humidity, the thermochemical gasification process becomes inefficient as the heat of evaporation of the liquid eclipses the combustion vapor of the solid substrate. In these cases, gasification will require drying and pretreatment of biomass, adding a higher cost to the economics of the process. (Uribe 2022)

The large amount of heat required to dry the feed makes the process inefficient. The largest application of SCWG is in the gasification of biomass and organic waste for hydrogen production. The distribution of products from SCWG varies depending on process variables such as: temperature, residence time, concentration in the feed, particle size, reactor configuration and presence of catalyst. (Castiblanco and Cárdenas 2020)

1.2. SCWG technology in the region

SCWG technology has not been fully exploited until today. There are three SCWG pilot plants worldwide.

Table 1. SCWG pilot plants worldwide (Özdenkçi et al. 2020).

PLACE	OPERATION	CAPACITY (ton of wet biomass/day)
Verena-Germany	600 °C, 28 MPa	2.4
Hiroshima-Japan	600 °C	1
Pacific Northwest Laboratory	400 °C	0.6

In Ecuador, in 2018, the Geological and Energy Research Institute (IIGE) inaugurates the pilot plant for hydrogen production by SCWG from biomass and operates with flows of up to 25 ml/min at pressures and temperatures of up to 6000 psi. and 700 °C (IIGE, 2018).

Despite the existence of these pilot plants, SCWG technology is currently not commercialized on a large scale due to its high costs.

1.3. Economy and scaling

For the development and commercialization of SCWG, it will be necessary to carry out techno-economic evaluations (TEA) where the feasibility is evaluated from a technical and economic point of view, in addition to evaluating the profitability and cost optimization of the SCWG system (Chen et al. 2020).

The competitiveness of SCWG in the hydrogen production process will depend on the hydrogen production cost (HPC) and its comparison with different SCWG systems and traditional processes for hydrogen production. In addition to controllable factors such as system capacity, product performance and operating parameters, the economic benefits of SCWG will depend on the implementation of national incentives for clean energy production, as well as market prices, fuel consumption in the process and the final products. (Brijaldo, Castillo and Pérez 2021). The average HPC of different technologies for hydrogen production such as: water electrolysis, steam reforming, pyrolysis, biomass gasification is 3.81 \$/kg, while in the SCWG it is between 0.94 - 6.6 \$/kg, which makes it economically competitive (Chen et al. 2020). Currently there is no detailed information, and it is a topic that must be studied.

1.4. Kinetics

Kinetic models describe the composition of the syngas as a function of temperature and residence time. With the help of a kinetic model, it is possible to predict the evolution of the system over time, calculate the dynamics and the mass and energy balances, being essential for the design of reactors and equipment. Most SCWG kinetic models focus on calculating kinetic parameters and predicting total feed conversion. Studies have also been done to predict the composition and performance of synthesis gas. (Okolie 2021).

Regarding biomass, different studies have been carried out in the field of kinetic modeling and SCWG simulation as indicated (Chico Proaño, 2023). The lack of kinetic models that describe the SCWG of residual biomass makes it difficult to carry out pre-feasibility and technical and economic feasibility evaluations of processes that include the design of gasifiers that operate at supercritical water conditions (P and T). Likewise, it is necessary that this information is generated to develop alternatives that allow the scaling of SCWG technology and that facilitate the optimization of the process.

2. METHODOLOGY

The cellulose SCWG experiment was carried out for three temperatures and a fixed reaction time, then the liquid products were separated from the gaseous ones, the products obtained were analyzed and with this information, through the integrated kinetic equations, the kinetic parameters of the gasification reaction were found.

2.1. Possible reactions

Among the possible reactions and sub reactions that occur in the biomass SCWG process there are known:

Steam reforming 1

$$C_6H_{10}O_5 + 7H_2O \rightarrow 6CO_2 + 12H_2 \tag{1}$$

Steam reforming 2

$$C_6H_{10}O_5 + H_2O \rightarrow 6CO + 6H_2 \tag{2}$$

Lactic acid formation

$$C_6H_{10}O_5 + H_2O \rightarrow 2C_3H_6O_3 \tag{3}$$

Glucose formation

$$C_6H_{12}O_6 + H_2O \rightarrow 2C_3H_6O_3 \tag{4}$$

Water-gas shift reaction (WGSR)

$$CO + H_2O \leftrightarrow H_2 + CO_2 \tag{5}$$

CO_2 methanation

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \tag{6}$$

CO methanation

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \tag{7}$$

In the steam reforming reaction, biomass degradation products such as phenolics react in the SCWG and decompose into CO, CO_2 y H_2. The reforming reactions produce CO, CO_2, H_2, and in the methanation and hydrogenation reactions CH_4 is produced. (Reddy et al. 2014; Li, H. et al., 2022)

2.2. Experimental design

For the experimental design, a sample of pure cellulose was used, and the SCWG was carried out at three different temperatures: 372 °C, 374 °C and 376 °C, obtaining final concentrations of the SCWG reaction products for a reaction time of 15 min. These temperatures were set to analyze the effect of temperature (independent variable) around the critical point of water, as well as its influence on hydrogen production (dependent variable).

2.3. Procedure

SCWG equipment is composed of feed pumping system, feed preheater, reactor/gasifier, gas-liquid separator. For the experimental process: water along with the biomass is pumped by the HPLC system under pressure into the reactor. The reactor is located inside an oven provided with electrical resistances inside that heat the feed to temperatures of 372 °C, 374 °C and 376 °C for a reaction time of 15 min for each case. Once the process is finished, the products obtained pass through the gas-liquid separator and are analyzed by gravimetry and liquid and gas chronography.
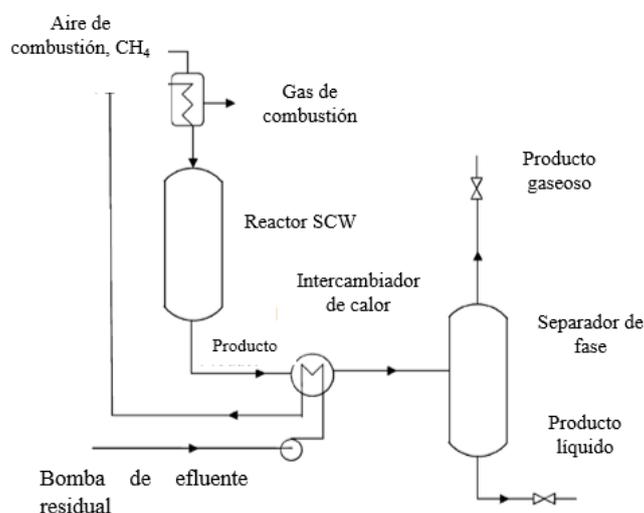

Figure 2. SCWG Equipment. (Basu 2010)

2.4. Volumetric flow rate calculation

The volume of fluid circulating per unit of time is calculated.

$$v_0 = \frac{V\,(ml)}{t\,(min)} \tag{8}$$

where:
v_0: volumetric flow rate.
V: reactor volume.
t: reaction time.

2.5. Residence time calculation

$$\tau = \frac{V\,(ml)}{v_0\left(\frac{ml}{min}\right)} \tag{9}$$

where:
v_0: volumetric flow rate.
V: reactor volume.
τ: residence time.

2.6. Reaction order calculation

Considering the reaction:

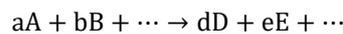$$aA + bB + \cdots \rightarrow dD + eE + \cdots$$

Table 2. Integrated Velocity Equations. (Liu, 2017)

ORDER 0	ORDER 1	ORDER 2
$-\dfrac{1}{a}\dfrac{d[A]}{d\tau} = k$	$-\dfrac{1}{a}\dfrac{d[A]}{d\tau} = k[A]$	$-\dfrac{1}{a}\dfrac{d[A]}{d\tau} = k[A]^n$
Separating the variables		
$d[A] = -a\,k\,d\tau$	$\dfrac{d[A]}{[A]} = -a\,k\,d\tau$	$-\dfrac{d[A]}{[A]^n} = a\,k\,d\tau$
Integrating between starting conditions: $([A]_0)$ Corresponding to arbitrary time t: $([A]_\tau \equiv [A])$		
$\displaystyle\int_{[A]_0}^{[A]} d[A] = -a\,k\int_0^\tau d\tau$	$\displaystyle\int_{[A]_0}^{[A]} \dfrac{d[A]}{[A]} = -a\,k\int_0^\tau d\tau$	$-\displaystyle\int_{[A]_0}^{[A]} \dfrac{d[A]}{[A]^n} = -a\,k\int_0^\tau d\tau$
Integrated equation		
$[A] = [A]_0 - a\,k\,\tau$	$ln\dfrac{[A]}{[A]_0} = -a\,k\,\tau$	$\dfrac{1}{[A]^{n-1}} - \dfrac{1}{[A]_0^{n-1}} = (n-1)a\,k\,\tau$
$k = \dfrac{C_{A_O}-C_A}{\tau}$	$k=\dfrac{ln\frac{C_{A_O}}{C_A}}{\tau}$	$k=\dfrac{c_{A_o}^{1-n}-c_A^{1-n}}{(1-n)\tau}$

For the calculation of the kinetic parameters, the integrated kinetic equations were used to determine the reaction order 0,1,2.

Order 0
$$k = \frac{C_{A_O}-C_A}{\tau} \tag{10}$$

Order 1
$$k=\frac{ln\frac{C_{A_O}}{C_A}}{\tau} \tag{11}$$

Order 2
$$k = \frac{C_{A_o}^{1-n} - C_A^{1-n}}{(1-n)\tau}$$
(12)

2.7. Activation energy calculation

To determine the kinetic parameters, the Arrhenius equation is used and graphed $\ln k\ vs\ \frac{1}{T}$.

Where:

k: speed constant.

A: pre-exponential factor.

R: universal gas constant.

Ea: energy activation.

$$k = Ae^{\frac{-Ea}{RT}}$$
(13)

By linearizing the equation, we obtain:

$$lnk = \frac{-Ea}{R}\frac{1}{T} + lnA$$
(14)

3. RESULTS AND DISCUSSION

Among the results obtained, two sections can be highlighted: the experimental part where the concentrations of the SCWG products were obtained and the subsequent treatment of the data for the determination of the kinetic parameters.

Table 2 indicates that as a result of the SCWG reaction of cellulose, gaseous products were obtained: CO, CO_2, CH_4, H_2, liquid or solution products: lactic acid, glucose and solid products: untransformed cellulose.

Table 3. SCWG results. Experimental data.

T		Liquids			Gases			Solids		V
°C		Lactic Acid	Glucose	H_2	CH_4	CO	CO_2	Initial cellulose sample	Final sample	
		g/L	g/L	% (v/v)	% (v/v)	% (v/v)	% (v/v)	g	g	ml
376	Repetition 1	0.482	0.015	0.904	0.131	12.599	4.776	1.013	0.229	334
	Repetition 2	0.368	0.090	0.825	0.208	11.489	6.655	1.074	0.234	299
374	Repetition 1	0.257	0.103	0.525	0.107	25.707	8.441	1.016	0.253	254
	Repetition 2	0.250	0.046	0.613	0.111	31.343	7.234	1.015	0.249	274
372	Repetition 1	0.083	0.210	0.309	0.115	17.886	2.982	1.001	0.264	266
	Repetition 2	0.106	0.183	0.274	0.105	16.947	5.074	1.004	0.255	248

Note.

T (Total)

V (Total volume of liquid collected at the end of the test)

3.1. Solid products (cellulose)

As seen in Figure 3, as the temperature increases from 372 °C to 376 °C, the grams of cellulose in the final sample decreases by 0.028 g, which indicates that at higher temperatures a greater conversion of cellulose into products occurs liquid and gaseous.
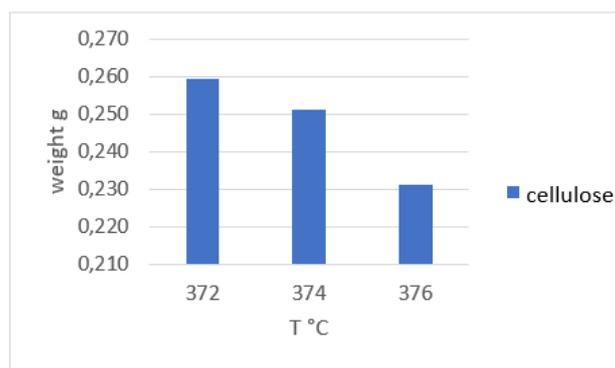
Figure 3. Final cellulose sample.

3.2. Liquid products (lactic acid, glucose)

As a result of the SCWG, liquid products with high added value were obtained, among which lactic acid and glucose stand out. As can be seen in Figure 4, lactic acid increases its concentration 4.5 times when going from subcritical temperature (372°C) to supercritical temperature (376°C) for a reaction time of 15 min. Glucose, for its part, shows an opposite behavior, decreasing by 26.9% when going from the subcritical temperature of 372 °C to the supercritical temperature of 376 °C, which indicates that steam reforming and gas-water shift reactions are favored.
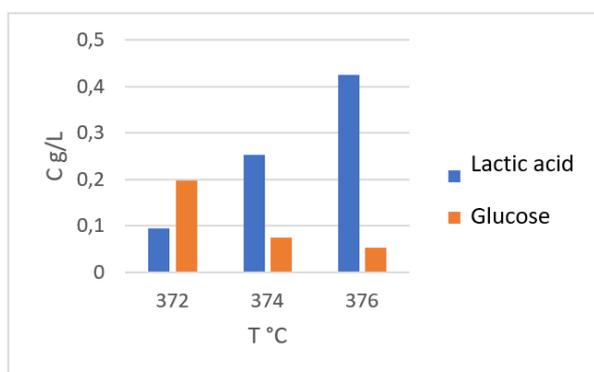

Figure 4. SCWG Liquid Products: Lactic Acid, Glucose.

3.3. Gaseous products (H_2, CH_4, CO, CO_2)

Regarding gaseous products, as indicated in Figure 5, CO and CO_2 were obtained to a greater extent, indicating that for a reaction time of 15 min, gas-water displacement reactions are favored, in addition to steam reforming. (Ec. 1,2,5).
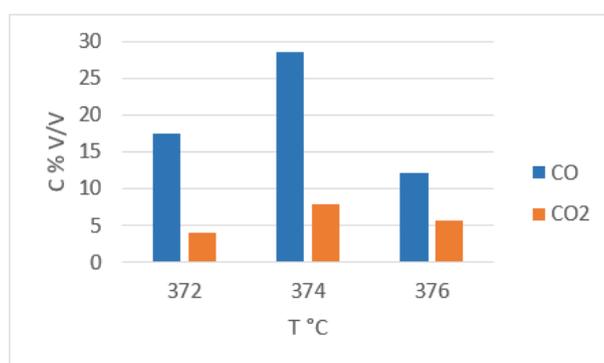

Figure 5. SCWG Gaseous Products: CO, CO_2.

One of the products of greatest interest obtained is H_2 due to its high potential for generating clean energy. As observed when going from subcritical temperatures (372 °C) to supercritical temperatures (372 °C), H2 increases its concentration in the products by 1.5 times, for a reaction time of 15 min.
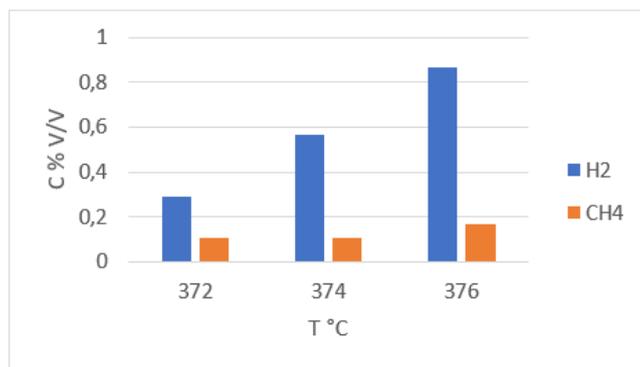

Figure 6. SCWG Gaseous Products: CH_4, H_2.

The increase in lactic acid, as well as the increase in hydrogen in the products, can be explained since at subcritical temperatures a greater formation of char and tar occurs when the biomass is partially decomposed. (Okolie 2021).

By using equations 10,11,12, the deviation values of k were obtained for each assumed reaction order. As Table 4 indicates, the smallest deviation from the kinetic constant occurs for zero order; however, when using a very diluted sample at 2%, it could be considered independent of the concentration. When comparing the results with different studies referring to the order of biomass reaction in SCWG, they mostly determine that biomass follows first-order kinetics as indicated (Yakaboylu et al. 2015), so it will be defined as a first-order reaction.

Table 4. Deviation of constant k in cellulose SCWG reaction.

	Standard Deviation		
Temperature	**Order 0**	**Order 1**	**Order 2**
376 °C	0.000134543	0.001328868	0.16803544
374 °C	6.12273E-05	0.000717012	0.293857155
372 °C	7.29719E-05	0.001070489	0.711952064

As indicated in Table 5, the kinetic constant increases as the temperature decreases, as does the reaction rate, which would imply that cellulose does not follow Arrhenius behavior at these conditions.

Table 5. Kinetic constant and reaction rate for each temperature.

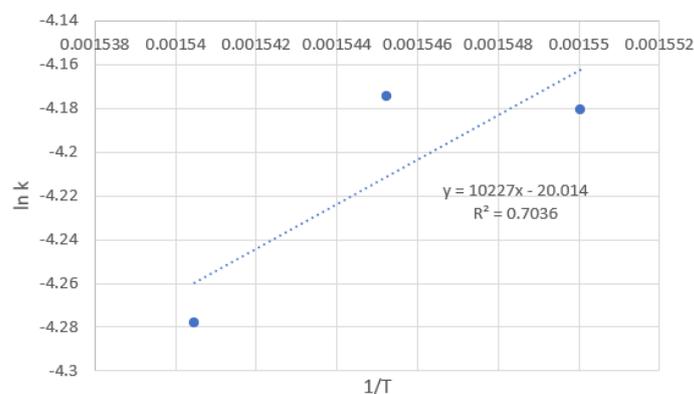| **TK**	**k**	**r [mol/L min]**
649.15	0.013865958	0.000454303
647.15	0.015380383	0.000547276
645.15	0.015290456	0.000562053

Figure 7. Arrhenius graph lnk vs 1/T

From the graph, Arrhenius Eq. (15) is determined, from which the kinetic parameters will be obtained.

$$lnk = 10227\frac{1}{T} - 20.014 \tag{15}$$

Table 6. Kinetic parameters.

R [J/mol K]	8.31
m	10227
Ea [kJ]	-84.986
A min⁻¹	-1.98033E-09

Regarding the kinetic parameters, as indicated in Table 5, the activation energy and the pre-exponential factor are negative, which can be explained by different causes:

- Being close to zero, the reaction occurs spontaneously.
- Conditions under which the experimentation was carried out: the use of a very short temperature range of (372 °C – 376 °C), a single reaction time of 15 min, very diluted initial sample, accumulation inside the reactor.
- The negative activation energy may indicate that, within the biomass gasification process in supercritical water, different complex sub reactions occur in which, if the reaction is ionic in nature, a change in the dielectric constant and the ionic product significantly affects the stability of the ions in the reaction and as a result, deviations from Arrhenius behavior can be expected. as indicate (Yong and Matsumura 2012).

CONCLUSIONS

As products of interest, lactic acid was obtained as it is a product with high added value and hydrogen due to its high energy potential. The concentration of hydrogen and lactic acid in the products increases by 1.5 and 4.5 times respectively as the temperature increases from subcritical (372 °C) to supercritical (376 °C).
The kinetic study of biomass gasification in supercritical water by integrated rate equations determined that the reaction follows a first-order behavior for temperatures of 372 °C, 374 °C and 376 °C. It was determined that the value of the kinetic constant for temperatures of 376 °C, 374 °C, 372 °C is: k_1=0.01386 min^{-1}, k_2= 0.01538 min^{-1} y k_3=0.01529 min^{-1} respectively.

By applying the Arrhenius equation, the kinetic parameters were calculated, determining a pre-exponential factor of -1.980E-09 min⁻¹ and an activation energy of: -84.986 kJ/mol.

Authors suggest performing studies in the presence of catalysts to determine their influence on the efficiency of the biomass SCWG process. They also recommended performing an economic analysis of the supercritical water gasification process, to ensure the viability of a large-scale process. A kinetic study for different types of biomass and different concentrations to analyze their influence on hydrogen production in the SCWG process is also necessary. Using a kinetic model different from Arrhenius better fit the biomass gasification process in supercritical water.

To obtain a more significant hydrogen concentration in the products, it is recommended to increase the reaction time and use of a wider range of supercritical temperatures as indicated in Okolie (2021).

Conflict of interest statement

The authors declare that there are no potential conflicts of interest within this research, authorship, and/or publication of this article.

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