A DETAILED KINETIC STUDY OF PYROLYSIS AND OXIDATION OF GLYCEROL (PROPANE-1,2,3-TRIOL)

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Abstract

Glycerol (propane-1,2,3-triol) has been the object of renovated interest in recent years. The production of biodiesel from transesterification of renewable biological sources such as vegetable oils and animal fat oils yields a considerable amount of glycerol (10%wt). The continuative increase in the biodiesel market therefore demands that a profitable use of glycerol is implemented. Similarly, the recent interest in the production of H_2 and syngas from bio-oils (the liquid organic fraction collected after the thermal processing of biomass material) has renewed the interest in glycerol. Furthermore, glycerol can be considered as a representative compound for the tar components derived from the carbohydrate fraction of biomass. Kinetic models that describe the thermal degradation of glycerol towards lighter hydrocarbons and non condensable gases are considered beneficial to an effective implementation of processes for its valorization. Aim of this work is therefore to analyze and discuss the primary propagation reactions of glycerol, together with the ones of acetol (1-hydroxypropan-2-one) and 3-hydroxypropanal (the primary products of glycerol). This kinetic model is then validated in comparison with three independent sets of experimental measurements. The first one refers to pyrolysis experiments at intermediate temperatures, while syngas is obtained from glycerol pyrolysis at higher temperatures in the second one. Finally the model is further validated in comparisons with experiments on combustion of droplets of propanol–glycerol mixtures.

Introduction

Glycerol (propane-1,2,3-triol) is an oxygenated organic compound that has been successfully and widely used in the chemical industry in the last decades. Major applications of glycerol can be found in the detergency industry, as well as in drugs and pharmaceuticals productions [1]. Other relevant usages of glycerol are summarized in Figure 1, which represents the market for glycerol in terms of %volumes in industrial use.
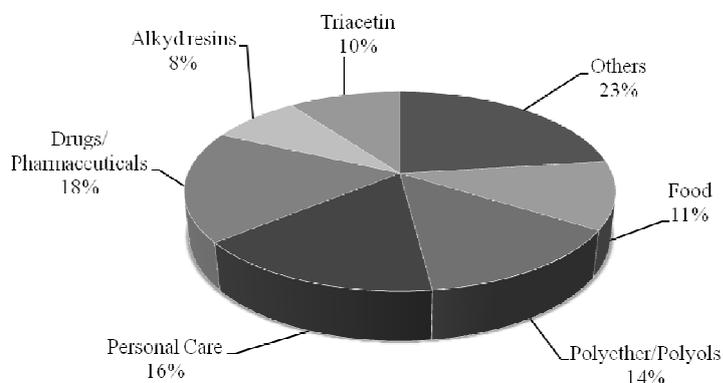

Figure 1: the market for glycerol. Adapted from [1].

Glycerol has been traditionally synthetised from chlorine and propylene, via an epichlorohydrin intermediate [2]. However, in recent times the increase in the production of biodiesel has resulted in a relatively large surplus of glycerol [3] , which is formed as a by-product. The production of biodiesel, indeed, goes through the transesterification of renewable biological sources such as vegetable oils and animal fat oils with an alcohol using alkaline or acid catalysts [4, 5]. The process yields 1 mole of glycerol for every three of fatty acid methyl esters (FAME) [6], with the crude glycerol attaining 10%wt of the overall product fraction [7]. The production of biodiesel is expected to grow in the near future: the figure indicates a probable production of 3.23 million tons worldwide, which would put an extra 323000 tons of glycerol on the market [1]. This would represent an increase of roughly 40% in the global glycerol market, which was estimated to be around 800000 tons in 2005. A profitable exploitation of glycerol is therefore crucial: this would promote the biodiesel industry, and decrease in price (from 850 USD/ton to 770 USD/ton according to [1]) could potentially transform glycerol in a platform chemical for various applications. The opportunity for glycerol as a reactant in several catalytic processes for the production of commodities has been reviewed in the recent literature [1]. Glycerol is also widely used as a feedstock for the production of acrolein [8], hydrogen [9], or synthesis gas [10], and eventually additional transportation fuels via Fisher-Tropsch synthesis [11]. Crude glycerol from the biodiesel process often contains many impurities and is a very poor fuel, which cannot be directly used in either petrol or diesel engines [12]. However, one mole of glycerol can theoretically produce up to 4 mol of hydrogen gas, and 3 mol of CO as gaseous products. Pyrolysis, gasification or steam reforming could lead to successful performances. Hydrogen production from the steam reforming reaction of glycerol over ceria-supported Ir, Co and Ni catalysts was studied [13]. Similarly, the reforming of glycerol and its aqueous solution over a nickel-based catalyst was investigated [14]. The gas phase pyrolysis of glycerol in steam in a laminar flow reactor has been successfully reported in [15]. Syngas production from the pyrolysis of glycerol in N_2 in a packed bed tubular reactor was also performed [16]. The thermal decomposition of glycerol in near-critical and supercritical water was also carried out by [14]. The pyrolysis of the crude glycerol from a biodiesel production plant was investigated by thermogravimetry coupled with Fourier transform infrared spectroscopy in a recent work [6].

The study of glycerol also goes in the direction of the demand for new energy sources and processes. It was successfully demonstrated that hydrogen can be produced from sugars and alcohols at temperatures near 500K in a single-reactor aqueous-phase reforming process using a platinum-based catalyst [16]. Similarly, the production of renewable hydrogen by autothermal steam reforming of volatile carbohydrates is accounted for in [17]. Methanol, ethylene glycol, glycerol and their solutions in water were studied using a platinum- and rhodium-based catalysts supported on alumina foams. These findings are of outstanding importance, when considering that the above mentioned carbohydrates, and products of further decomposition (glycerol, for instance) can be derived from the thermal processing of biomass material, representing indeed the products of the so-called secondary phase of biomass thermal decomposition [18]. Data showing that the yield of H_2 obtained from both pyrolysis liquid and crude glycerol are close to 80% of the stoichiometric value are reported [19], which represents an interesting opportunity. A detailed account of the products of biomass decomposition appears to be necessary. Usually very simplified representations of tar formation and conversion are adopted. Most work in the area of combustors and gasifiers simply refers to global reactions [20]. However, efforts in the direction of a kinetic approach that chooses a limited set of primary reference species to represent and describe the primary tar, released during devotalization (e.g. levoglucosane, xylan, hydroxyl-acetaldehyde, acetol, anisole and substituted phenols, benzene, toluene and naphthalene), and proposes a multistep

kinetic model of biomass pyrolysis can be found in literature [21]. In addition to the primary reactions of reference tar lumps, the kinetic scheme accounts for the interactions between the lumps and the surrounding gases. A general and detailed kinetic scheme of pyrolysis and oxidation of hydrocarbon fuels is applied to this purpose [22]. Validation of the proposed kinetic scheme, with specific reference to the production of bio-oils, was performed and offered good results, particularly in terms of product yields [23]. Within this perspective, this work aims at broadening the horizon of prediction of the referenced model, by specifically detailing the secondary reactivity of glycerol, a model compound for the tar fraction originated by carbohydrates present in biomass feedstocks. The major reactive steps in the pyrolysis of glycerol are described in the following. Particular consideration is given to the H-abstraction reactions, with reference to the different types of hydrogen atoms available in the glycerol molecule. Molecular dehydrations appear to be interesting reaction pathways as well. The model is tested against several sets of experimental data, offering good agreement between predicted and measured values.

Primary propagation reactions of glycerol, acetol and 3-hydroxypropanal
Table 1 summarizes the initiation and primary propagation reactions of glycerol.

Table 1. Primary propagation reactions of glycerol, acetol, and 3-hydroxypropanal.

	GLYCEROL: C3H8O3 (CH2OH-CHOH-CH2OH) 1,2,3-propanetriol		
	Reactions	A [1/s]	Eatt [cal/mol]
1	GLYCEROL > CH2OH+H+CH2OHCHO	1.00E+16	80000
2	GLYCEROL > CH2OH+OH+CH3CHO	1.00E+16	80000
3	R + GLYCEROL > RH+ OH + C3H6O2	4 H primary alpha	
4	R + GLYCEROL > RH+ OH + ACETOL	1 H secondary alpha	
5	R + GLYCEROL > RH+ CH2OH + CH2OHCHO	1 H oxydril, secondary C	
6	R + GLYCEROL > RH+ CH2O + OH + CH3CHO	2 H oxydril, primary C	
7	GLYCEROL = ACETOL + H2O	4.00E+13	65000
8	GLYCEROL = C3H6O2 + H2O	2.00E+13	65000
	ACETOL: C3H6O2 (CH3-CO-CH2OH) 1-hydroxypropan-2-one		
	Reactions	A	Eatt
9	ACETOL = CH2OH + CH3CO	1.00E+16	80000
10	ACETOL > CH2OH + CH3 + CO	1.00E+16	80000
11	R + ACETOL > RH + CH2CO + CH2OH	3 H primary	
12	R + ACETOL > RH + CH3 + CHOCHO	2 H primary alpha	
13	R + ACETOL > RH + CH2O + CH3CO	1 H oxydril, primary C	
14	ACETOL = CH3CHO + CH2O	2.00E+13	53000
	C3H6O2: (CHO-CH2-CH2OH) 3-hydroxypropanal		
	Reactions	A	Eatt
15	C3H6O2 = CH2CH2OH + HCO	1.00E+16	82000
16	C3H6O2 = CH2OH + CHOCH2	1.00E+16	81000
17	R + C3H6O2 > RH + CH2CH2OH+ CO	1 H acylic	
18	R + C3H6O2 > RH + CH2CHCHO+ OH	2 H secondary	
19	R + C3H6O2 > RH + CH3CHO + HCO	2 H primary alpha	
20	R + C3H6O2 > RH + CH2O + CHOCH2	1 H oxydrilic, primary C	
21	C3H6O2 = CH2CHCHO + H2O	2.00E+13	51000
22	C3H6O2 = CH3CHO + CH2O	2.00E+13	54000

The initiation paths involve either the cleavage of a C-C bond (1), or the cleavage of a C-O terminal bond (2), with the consequent formation of, respectively, hydroxyacetaldehyde and acetaldehyde, together with smaller radicals. As in most of the radicalic reaction schemes, the

propagation reactions are of major interest. Particularly, the abstraction of hydrogen on the original glycerol molecule can lead to the formation of either acetol or 3-hydroxypropanal, which represent important primary intermediates. These compounds can undergo further reactions, which are reported in Table 1. The further decomposition and/or oxidation reactions of smaller radicals and molecules are already described elsewhere [22, 24, 25]. The overall kinetic scheme is based on hierarchical modularity and is constituted by more than 300 species involved in more than 7000 reactions. The complete mechanism in CHEMKIN format is available online (www.chem.polimi.it/CRECKModeling/).

The H-abstraction or metathesis reactions are systematically described in their general form in (1):

$$R + GLYCEROL > RH + RC_3H_7O_3 \tag{1}$$

where R and RH stand respectively for all the possible H abstracting radicals and for the corresponding saturated species. The molecule of glycerol contains 8 hydrogen atoms, that can be divided and classified into 4 primary H-atoms in α position, 1 secondary H-atoms in α position, and 3 hydroxyl H-atoms. The metathesis reactions, therefore, can possibly lead to the formation of four different radicals, corresponding to the general formula of $RC_3H_7O_3$. These radicals, however, are not explicitly mentioned in the kinetic scheme, as a rapid evolution is envisaged, leading to an enolic organic, and a smaller radical. The enolic compounds, moreover, are easily converted in their tautomeric aldehydic forms, which are listed as the final products of the metathesis reactions in Table 1. The extended mechanism of the H-abstraction reactions (3-6) is represented in Figure 2. The formation of the $RC_3H_7O_3$ radical is expected to be the rate determining step, which determines the kinetic constant for the process.
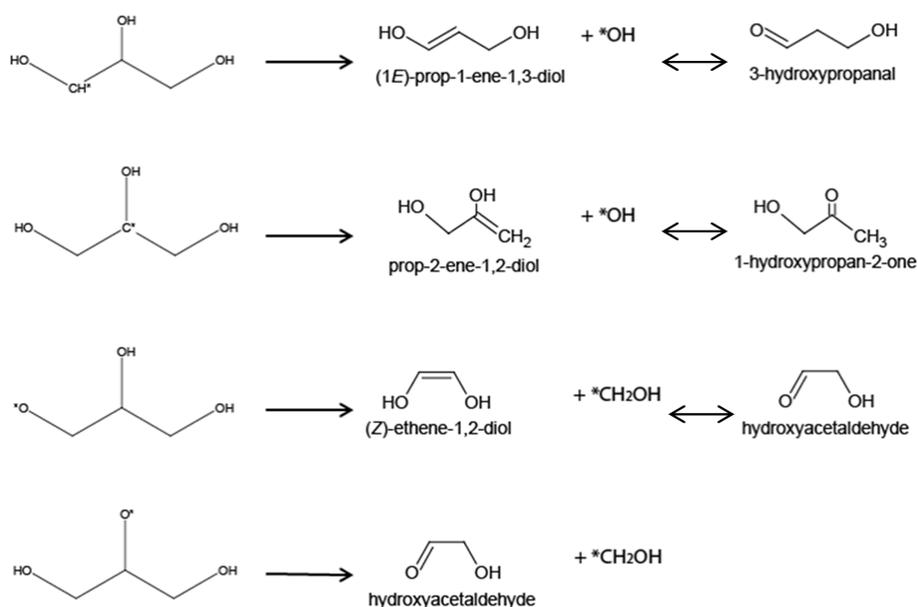

Figure 2. Primary radicals from H-abstraction of glycerol, and their further rearrangements.

Rate constants for the H-abstraction reactions

As suggested above, the H-abstraction reactions plays an important role in the reactive system, therefore a careful account of their kinetic constants should be given. In a recent work [26], electronic structure methods have been used to calculate the kinetic constants for H-

abstraction reactions from alcohols. As stated by the authors, this approach enables to estimate with good accuracy the rate constants for small reactants, and to extend the results to the corresponding reactions of larger compounds containing the same functional groups, through the application of proper estimation rules. The reactivity of butanol and its isomers has been studied as well in a previous work of our research group [25], and the two results were found to be in good agreement. Table 2 summarizes the above mentioned results.

Table 2. Kinetic constants for H-abstraction reactions according to [26] and [25].

Type of H atom	Kinetic constants [26] $[cm^3mol^{-1}s^{-1}]$, T in [K]	Kinetic constants [25] $[cm^3mol^{-1}s^{-1}]$, T in [K]
Hydroxyl	$3.6 \times 10^6 \times T^{2.11} \times exp(-9830/R/T)$	$1.7 \times 10^6 \times T^2 \times exp(-6525/R/T)$
Primary α-C-H	$2.7 \times 10^6 \times T^{2.16} \times exp(-4140/R/T)$	$3.6 \times 10^6 \times T^2 \times exp(-3950/R/T)$
Secondary α-C-H	$2.4 \times 10^7 \times T^{1.88} \times exp(-2460/R/T)$	$3.6 \times 10^6 \times T^2 \times exp(-2660/R/T)$

The tabled values refer to a single abstraction, the overall kinetic constant should therefore be multiplied by the number of H atoms of the selected type that are present in the original molecule. A comparison of the values in the temperature range of interest for the pyrolysis of glycerol (i.e. 900-1100K) shows that they are in very good agreement. The rate constants that our research group proposed in [25], and were confirmed with comparison to [26], were used to perform simulations in the present work. It can be interestingly noticed that the rate of reaction for the abstraction of an hydroxyl hydrogen is approximately close to 70% of the rate of removal of a primary H atom from a methyl group. On the other hand, the removal of hydrogen from the α carbon atoms (both primary and secondary) is almost 50% higher than the rate values of the corresponding removal of H atoms from alkanes. The enhanced reactivity related to the effect of the OH group on the reactivity of neighboring C-H bonds is negligible when considering carbon atoms in β-position. The extension of this rule to the generalized case of the presence of more than one OH group (as, for instance, in glycerol) is suggested from a series of data on ethylene glycol [26].

Molecular dehydration reactions
As already observed in previous works on alcohol fuels [25, 27], molecular dehydration is an important reaction class in biomass pyrolysis. Several dehydration reactions are reported in Table 1, for both glycerol and its primary intermediate products. The different nature of simple alcohols seems to have little impact on the reference rate value for this reaction class [26]. On the contrary, significantly larger deviations are observed for substituted aldehydes, when water elimination yields products with conjugated double bonds. This is typical, for instance, of 3-hydroxypropanal and acetol. As clearly shown in Table 1, the rate constants for these reactants are consistently larger than the ones estimated for saturated alcohols, according to the above mentioned approach of generalization through estimation rules. In other words, the aldehyde moiety influences the reactivity by stabilizing the transition state and the products [26]. This stabilizing effect is traduced in an activation energy of the process which is roughly 10 kcal/mol lower than the corresponding alcohol. Figure 3 represents the major dehydration pathways for glycerol, 3-hydroxypropanal ad acetol (1-hydroxypropan-2-one).
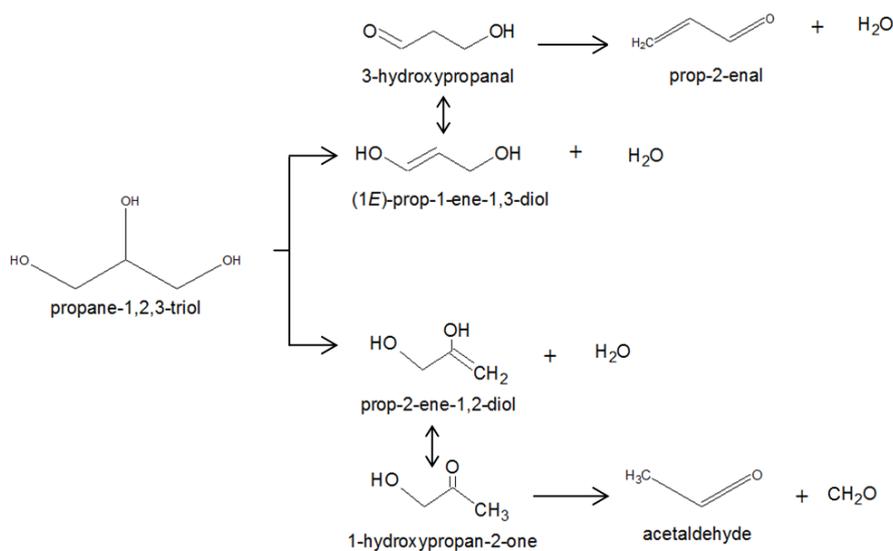
Figure 3. Dehydration reactions of glycerol, 3-hydroxypropanal and acetol.

Model validation and comparisons with experimental measurements

The kinetic model of glycerol pyrolysis described in the previous section is validated in comparison with three independent sets of experimental measurements. The first one refers pyrolysis experiments performed at intermediate temperatures [15], while in the second one glycerol is pyrolysed at high temperatures for the production of syn gas [16]. Finally the model is further validated in comparisons with experiments on combustion of droplets of propanol–glycerol mixtures [28].

Pyrolysis of glycerol at intermediate temperatures

Pyrolysis of the glycerol in steam mixture was analyzed in a tubular, laminar flow quartz reactor [15]. After a rapid preheat (residence time ~0.015 s), a steady flow of a glycerol in steam mixture enters the isothermal zone of the reactor, which is characterized by a relatively small surface to volume ratio (ca. 5 cm^{-1}), and residence times of ~0.1 s. Due to the short residence time, only 15% of the initial glycerol decomposes at 650°C, while at 750°C glycerol is almost completely converted. At high temperatures, there are significant successive decomposition reactions of the primary products. This indicates that, if the major interest of the process is in maximizing bio-oil production, the optimal temperature range is 650-700°C. A comparison between the experimental results of [15] and the predicted values obtained with the proposed kinetic mechanism is reported in Table 3. The results show a satisfactory agreement between experimental data and model predictions. Particularly, the major products of the pyrolysis reaction are acrolein and acetaldehyde. The simulations seem to shift the peak of production of both at higher temperatures with respect to the experimental results. This goes with the fact that there is no experimental evidence of the reaction intermediates of acetol and 3-hydroxypropanal. A possible explanation of these facts is the following : on one hand, recent studies [26] suggest that the second dehydration of glycerol (yielding acrolein and acetaldehyde) is strongly favoured with respect to the first one, which leads to acetol and 3-hydroxypropanal. Figure 4 proposes the predicted concentration profiles of the major species involved in the reaction system, and a clear intermediate behaviour is visible for both acetol and 3-hydroxypropanal. On the other hand, the detail of the experimental results is limited, and the proximity (both in terms of structure, and particularly of C-groups) of the investigated compounds is likely to make a precise distinction complex.

Table 3. Products of the pyrolysis of glycerol in steam at 650-675-700 °C and 1 atm.

Temperature	650°C		675°C		700°C	
	EXP	SIM	EXP	SIM	EXP	SIM
Glycerol (Mole%)	1.69	1.69	0.9	0.9	1.04	1.04
Conversion	17.6	17.7	34	27.4	25	24.2
Residence time [s]	0.13	0.13	0.13	0.13	0.048	0.05
Products Yield (%)						
Acrolein	52	38.6	39	38.2	34	38.7
Acetol	-	13	-	6	-	7.7
3-hydroxypropanal	-	9	-	3.3	-	4.4
Acetaldehyde	48	28.2	38	35.6	42	34.3
CH2O	-	28.8	-	34.9	-	34.2
CO	-	10.8	35	19.1	58	16
CO2	-	0.96	0.3	1.7	1	1.4
Hydrogen	-	13	29	14.5	44	13
Methane	-	2	5	3.8	11	3

A similar consideration can be put forward with respect to formaldehyde: as stated in the original work [15], a quantitative detection was difficult, due to the modest concentration (original glycerol is highly diluted in steam as well). The decomposition of formaldehyde to CO and H_2 in the product stream can also be envisaged, and would explain the low yields of both in the simulations, together with the simulated data on formaldehyde, which appear to have no correspondence in the experimentally detected products.
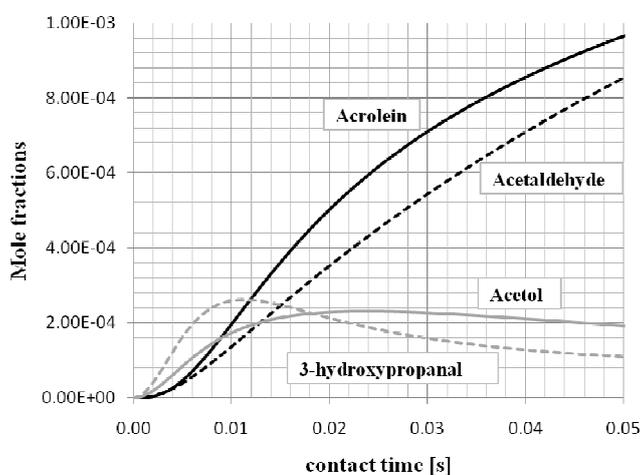
Figure 4. Major products from glycerol (1.69%) pyrolysis in steam at 700 °C and 1atm.

Syngas production at 900-1100 K

The pyrolysis of glycerol for the production of syngas, useful for instance as a feed stock for the Fisher-Tropsch synthesis to produce transportation fuel, is reported in recent literature [16]. The pyrolysis of glycerol was carried out at various temperatures (650–800 °C), and varying flow rates in a tubular reactor at atmospheric pressure, using different packing materials. The major product was syngas, in which traces of CO_2, CH_4 and C_2H_4 were also measured. Composition of product gas ranged between 70–93 mol% for syngas, 3–15 mol% for CH_4 and 2–12 mol% for C_2H_4. Correspondingly, the heating value of the gaseous product ranged from 13 to 22 MJ/m^3. Figure 5 shows a comparison of the experimental measurements and the model simulation results in terms of product yields. The liquid and gas yields show a good agreement, whereas the major deviation in the model description comes from the fact

that no char prediction is given. The carbonaceous residue found experimentally can probably be due to the successive polymerization of tar products that stick to the particle material within the reactor at low temperatures. Acrolein, for instance, is well known for its ability to polymerize at room temperature. These phenomena are not included in the gas phase reactive kinetic scheme that is used for simulation purposes. Table 4 shows a detailed comparison between experimental measurements and model predictions for the gas composition. The results obtained from the simulation are generally in good agreement with the reported experimental values. Particularly, syngas yields are correctly predicted. The only major deviation that demands some explanation is the discrepancies between the results for CH_4 and C_2H_4 at high temperature (800°C). Experimental results show a strong decrease in light hydrocarbons at high temperature, suggesting that their decomposition should take place, Moreover, the increase in the syngas yield seems to suggest that the steam reforming of methane is occurring within the reactor. However, these evidences find no matching in the simulation, on the contrary both cracking of light HC and steam reforming of methane are expected to become relevant in the homogeneous phase only at higher temperatures. A possible explanation of this discrepancy could come from an equilibrium calculation. Thermodynamic equilibrium indicates that at 800°C the most stable products in the system are CO and H_2, whereas methane and other hydrocarbons should decompose. If we admit that some catalytic effect is present in the reactor, then this could promote the steam reforming reactions of methane and ethylene:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{2}$$
$$C_2H_4 + 2H_2O \rightarrow 2CO + 4H_2O \tag{3}$$

and shift the final composition towards the equilibrium value, which sees the predominance of syngas. Evidence of analogous concerted heterogeneous-homogeneous processes are reported in literature [29]. Table 5 presents the final product distribution obtained by coupling the results of the simulation performed using the proposed kinetic mechanism for glycerol with the mentioned steam reforming reactions of methane and ethylene, for which a degree of conversion of 65% is assumed. Results show a very satisfactory agreement with the experimental data. It is also interesting to observe that the experimental data report the formation of a solid carbonaceous residue, which is not present in the simulation results. This deviation can be explained by taking into consideration the eventual polymerization of some intermediate pyrolysis products, for instance acrolein. The high surface-to-volume ratio in the reactor, together with the possible catalytic effect of the nickel-chrome alloy that constitutes the reactor tube, could enhance the formation of deposits on the walls.
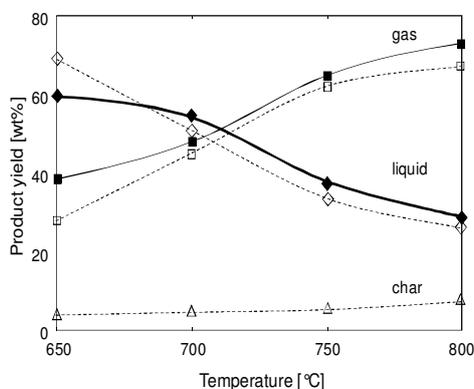

Figure 5. Effect of temperature on product yields during pyrolysis of glycerol. Experimental data (dashed lines and empty symbols) and model predictions (solid lines and symbols).

Table 4. Effect of temperature on gas product composition during pyrolysis of glycerol at carrier gas flow rate 50 mL/min.

Temperature [°C]	650		700		750		800	
Components (mol%)	EXP	MOD	EXP	MOD	EXP	MOD	EXP	MOD
H2	17	23.9	22.1	22.3	27.7	22.8	48.6	23.6
CO	54	41.4	50	45.2	45.7	46.4	44.9	47
CO2	0.2	4.8	0	3.9	1.1	3	1	2.4
CH4	14.2	10	14.5	13.3	14.1	14.7	3.3	15.7
C2H4	10.1	19.3	9.6	13.8	9.1	11.8	2	10.5
C2H6	2.2	0.7	2	1.6	1.5	1.2	0.1	0.8
C3H6	2.4	0	1.7	0	0.8	0	0.1	0
H2+CO	71	65.3	72.1	67.5	73.4	69.2	93.5	70.6

Table 5. Results corrected with the introduction of the steam reforming reactions.

Mole fractions	EXP	MOD	MOD + SR
H2	48.6	23.6	49
CO	44.9	47	43.1
CO2	1	2.4	1.47
CH4	3.3	15.7	3.6
C2H4	2	10.5	2.4
C3H6	0.2	0.8	0.5
H2+CO	93.5	70.6	92.1

Combustion of propanol–glycerol mixture droplets

To our knowledge, data on the combustion of glycerol in relatively simple systems are not available in literature to date, and therefore the validation of the proposed kinetic scheme for glycerol in oxidative conditions has limited opportunities. However, recent and useful data can be found on reduced-gravity experiments on combustion of propanol–glycerol mixture droplets, performed by Dee and Shaw [28] in air at standard temperature and pressure. Due to the high viscosity of glycerol, propanol/glycerol mixtures were investigated. This choice is justified with the scientific interest in propanol and alcohols as alternative fuels. It might be worthy noticing that glycerol can influence convective mixing rates inside droplets by reducing liquid convective flow velocities. Droplets were initially ~1 mm in diameter with initial glycerol mass fractions of 0.05 and 0.2. Experiments were conducted at the 2.2 s drop tower at the NASA Glenn Research Center. Droplets are dispensed onto a fiber and are ignited by a hot wire igniter with a controlled current.

Figure 6 shows that the square of the droplet diameter decreases linearly with time, i.e. the d^2 law is basically followed by both the droplets. Experimental flame standoff ratios (i.e., instantaneous ratios of flame and droplet diameters) are shown as well for times prior to flame contraction and after early ignition transients have decayed. Flame standoff ratios are nearly constant with values of ~5, indicating a quasi-steadiness of the region between the droplet and the flame. Computations have been performed following the numerical approach already discussed elsewhere [30], in which the conservation equations of mass, momentum, energyand chemical species are solved in the gas phase under the hypothesis of microgravity conditions. Numerical simulations are performed considering a diffusion coefficient equal to 10^{-8} m^2/s [28] for the liquid phase. Following the suggestions reported in [28], the liquid

diffusivity was increased by a correction coefficient, in order to account for the internal recirculations.
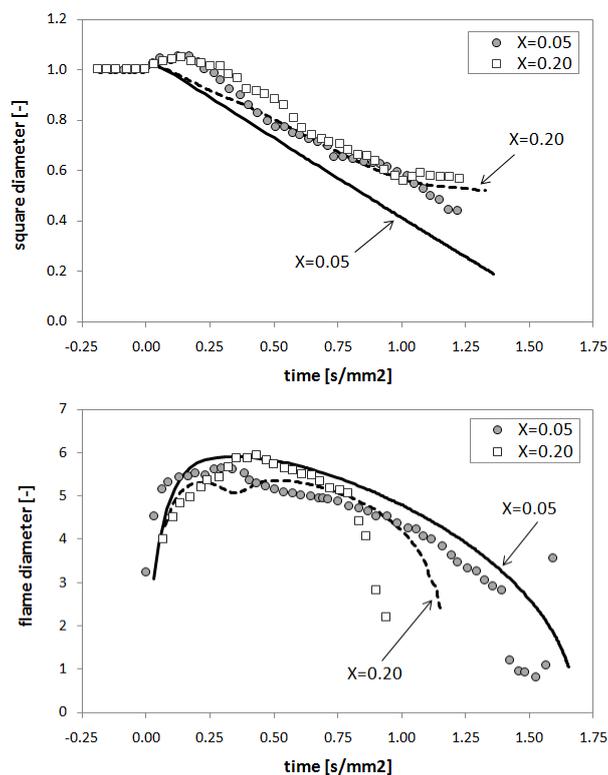

Figure 6. Histories for droplet and flames sizes with glycerol mass fraction 0.05 and 0.2. Symbols : experiments. Lines: model.

According to the performed calculations, the value of the correction coefficient that best fits the experimental data is ~4. The agreement between numerical results and experimental data is satisfactory: the flame stand-off ratio is well captured at every time and the vaporization rate is correctly predicted. The model is not able to describe the initial droplet growth (associated to the droplet heating), but this phase is strongly affected by the characteristics of the hot wire igniter and the heat transfer through the suspending fiber, for which additional data are necessary. The model can effectively predict the flame extinction observed in the experiments corresponding to an initial glycerol mass fraction of 0.20. The diameter of the droplet after extinction is accurately captured, whereas a delay in the estimated extinction time with respect to the experimental data is noticeable.

Conclusion

This work presents a model of the primary reactions of glycerol and of its primary products (acetol and 3-hydroxypropanal). Particular attention is paid to the H- abstraction reactions on the different hydrogens of the molecules. The study of the reactivity of the hydrogen atoms on the carbon in α position is emphasized as it show the enhancing effect of the neighboring hydroxyl group. Furthermore, the role of molecular dehydrations is discussed and the effect of the aldehyde moiety which is produced within the molecule from the first dehydration is underlined. The second dehydration of 3-hydroxypropanal to acrolein is indeed favoured, with a decrease in the activation energy of about 10 kcal/mol.

The proposed model is validated against experimental data found in literature. Pyrolysis of glycerol in steam, and pure glycerol for syngas production are considered. The model generally captures the system reactivity and the main product distribution. Major deviations

are taken into consideration, and catalytic effects of the reactor walls, together with limitations in the analytical details are invoked as contributions in the explanation. The capability of the mechanism to reproduce the combustion behavior of glycerol is tested against experimental data evinced from tests on droplets composed of a mixture of propanol and glycerol mixture, which were combusted in reduced-gravity. Despite the complexity of the system the model shows a good agreement with the measurements in term of the square diameter of the droplet, and flame diameter for different compositions of the mixture.

The importance of the proposed results is twofold. On one hand, there is a growing interest in a profitable exploitation of glycerol, due to its importance as the major by-product of biodiesel production. On the other hand, glycerol is an effective reference component for the intermediate components which can be formed from biomass pyrolysis and gasification, and consequently its investigation contributes to the identification of the main reaction classes involved in these processes and their kinetic parameters.

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