



Kinetics of Ethylene Glycol: The first validated reaction scheme and first measurements of ignition delay times and speciation data



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ABSTRACT

The reaction kinetics of Ethylene Glycol (EG) is studied, due to its similarity in chemical composition and physical properties, as a model fuel for pyrolysis oil. Recently, the combination of fast pyrolysis of residual biomass and subsequent gasification of the pyrolysis oil has gained high interest. In the gasification process, oxygen is often used as a gasifying agent (e.g. auto-thermal gasification) which led us to study EG under oxidation condition.

This study has experimental and modeling objectives: We obtain novel experimental data that we use for validation of our EG oxidation model that enable predictive modeling and optimization of gasifiers through multi-dimensional CFD simulations. Both, detailed and reduced skeletal models are obtained. The validation data needed for the model is studied in two different types of experiments namely, (1) ignition delay times obtained behind reflected shock waves in the temperature range of 800–1500 K at 16 bar and, (2) quantitative species profiles measured in a high temperature flow reactor setup for fuel equivalence ratios $\Phi = 1.0$ and 2.0 in the temperature range of 700–1200 K. Both experiments are performed in the EG-system for the first time providing the relevant basis for the understanding on how EG decomposes and for the optimization of the reaction mechanism. The influence of different product channels on the reactivity of the EG system is investigated and leads us to pose the question, if enol can be formed in this combustion (oxidative) environment.

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1. Introduction

Reaching for renewable alternative energy sources, fuels that are carbon neutral and ensure security of supply at affordable price are of high interest in the energy sector including the biomass-based fuels. In the EU, the current target of 20% final energy consumption from renewable sources by 2020 is already closing its goal with 15.3% projected in 2014. A renewed target is set to 27% by 2030 [1]. These targets are also part of the EU's energy and climate goals for 2030. Though the biomass based resources are renewable, their rate of regeneration is low. Therefore, to achieve maximum use, more efficient processes to convert biomass are required.

Energy densification is the major motivation behind the conversion of biomass to liquid fuels. As an example from Kolb et al. [2], a dry biomass with an energy density of 2 MJ/L can be converted by gasification to a syngas of 25 MJ/L. Through Fischer Tropsch (FT) processing, produced fuels features energy densities of approximately 36 MJ/L. Gasification of the pyrolysis oil is not

strictly a pyrolysis process. Especially, entrained flow gasification, which is often used in large scale devices, is an oxidative environment [3]. In auto-thermal gasifiers oxygen (or air) is often employed as a gasifying agent to supply heat to drive the overall endothermic process. Insertion of the gasifying agent depends on the type of gasifier used (in fluidized bed in 2nd phase after pyrolysis; in entrained-flow gasifiers in single stage at the start). In addition, understanding the reaction kinetics at a wide range of fuel stoichiometry is important as it has influence on the gasification efficiency and carbon conversion. The change in fuel stoichiometry would move the gasification to combustion thereby changing the product spectrum. Therefore, the focus of our work is on the oxidation of ethylene glycol (EG) including stoichiometric and rich conditions.

The pyrolysis oil entering a gasifier typically contains high amount of oxygen due to a variety of oxygen containing heteropolymer present in the original feedstock. The process occurring inside the gasifier is complex and involves multiphase chemistry. For computational fluid dynamics (CFD) study of a gasifier, one needs a reaction kinetic model. To this end, EG is selected as a model fuel for pyrolysis oil [3,4] based on its similarity in the chemical composition and physical properties. The unusual high content of oxygen (30–60 wt%) in pyrolysis oil is matched by the

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Table 1
Comparison of physical properties and chemical composition of pyrolysis oil obtained from different feedstock and EG.

Bio-oil	Properties							Composition (wt%)		
	Density (kg/m ³)	Dynamic Viscosity (cP)	Pour point (°C)	Flash point (°C)	Enthalpy of combustion (MJ·kg ⁻¹)	Acidity pH	H ₂ O Content (wt%)	C	H	O
Ethylene glycol [9]	1132 (20°C)	18–56 (0–24°C)	–12	111	16.96	–	–	38.7	9.7	51.6
BTG-BtL	1170	20–100 (50°C)	–	–	16–19	2.9	15–35	46	7	47
Pyrolysis oil [10]	1100–1300	40–100	–36––9	45–100	16–19	2.0–3.5	15–30	32–49	6–8	44–60
Bio-oil [11]	1250 (20°C)	–	–	–	17.51	2.0–3.8	15–30	60.6	7.7	29.2
Bio-oil [12]	–	–	–	–	–	–	10–30	47.5–56.8	7.0–8.5	31.3–45.2
From various feedstock [8]	–	–	–36––9	50–100	13–18	2.0–3.7	15–30	32–49	6.9–8.6	44–60
ASTM7544 [13]	1100–1300 (20°C)	–	–9	>45	>15	–	<30	–	–	–

two oxygen atoms present in the EG molecule. In addition to reasons on safety and price, EG is a single component surrogate providing a striking advantage for the reaction model development and also in terms of computational resources needed to perform CFD calculations.

The presented model is based on our previous work: a model of EG published by Hafner et al. [5,6]. This model, however, has not been sufficiently validated due to the lack of experimental data at the given time. At first, a revision of this mechanism was required mainly to reduce numerical stiffness. Due to the lack of any experiments in combustion environment, understanding of EG combustion chemistry was impossible. Therefore, a new set of validation experiments have been undertaken in the present work which has improved the previous understanding of the decomposition routes of EG.

This study provides an important reaction chemistry model for the computational gasification studies. The high temperature shock-tube experiments are performed for stoichiometric mixtures diluted in argon and at pressure of 16 bar. The atmospheric flow reactor measurements at intermediate temperature range and at two stoichiometries ($\Phi = 1.0$ and 2.0) provide the spectrum of intermediates and products formed during the oxidation process. These are used to validate the reaction model and understand the underlying chemistry of EG oxidation. A detailed comparison of fuel intermediates and their formation paths is described in the present work. In addition, a reduced skeletal mechanism is also presented comprising 43 species and 270 reactions to be used to speed up multi-dimensional CFD calculations (the Supplemental Material provides additional information on the reduced model validation). Thus this work presents the first validated reaction mechanism based on the first experimental investigations of ignition delay times and species profiles measured in a shock-tube and a flow reactor environment, respectively.

1.1. Ethylene Glycol – selection as pyrolysis oil surrogate

The biomass feedstock is converted to the pyrolysis oil prior to gasification. This pyrolysis oil, also referred as bio-syn crude oil, or simply bio-oil, is highly oxygenated and is highly viscous at ambient conditions. It possesses poor stability due to its high intrinsic oxygen content, usually 30 to 60 wt% [7,8], depending on the feedstock. This high oxygen content in pyrolysis oil stems from heteropolymers lignin, cellulose and hemicellulose present in the feedstock.

The selection of EG is based on its similar physical-chemical characteristics to the pyrolysis oil obtained from varying feedstocks. Typical physical properties and chemical composition of the pyrolysis oil obtained from different literature sources are summarized in Table 1. These properties vary by the extraction methods used and by the type of biomass from which they are extracted.

Table 1 also shows the properties of EG for a direct comparison and for its apparent selection and suitability as a pyrolysis oil surrogate.

The enthalpy of combustion of most hydrocarbon fuel ranges from 41–44 MJ·kg⁻¹ which is about twice as high as the heat obtained from the biomass combustion (about 13–18 MJ·kg⁻¹). The enthalpy of combustion of EG is about 17 MJ·kg⁻¹ making it suitable surrogate fuel for pyrolysis oil. In addition, the chemical composition of the pyrolysis oil depending on the source of the feedstock varies from 32–60 (wt%) carbon, 7–10 (wt%) hydrogen, and 30–60 (wt%) oxygen. The chemical composition of EG lies within this typical range. Similarly, liquid properties such as the density or the viscosity of EG are comparable to the properties of the pyrolysis oil. Thus, this comparison justifies the selection of EG as a suitable surrogate for the pyrolysis oil.

1.2. Ethylene Glycol – reaction kinetics

The molecule EG contains two hydroxyl groups attached to the ethane molecule and it is similar to ethanol (one less hydroxyl group). Therefore it is reasonable to assume that the decomposition of EG is similar to ethanol. The theoretical studies of Park et al. [14] showed that water elimination is the major path in ethanol decomposition ($C_2H_5OH \rightarrow C_2H_4 + H_2O$) with a 66.6 kcal·mol⁻¹ barrier. The only information available on the thermal decomposition of EG over a wide temperature and pressure range is a theoretical study from Ye et al. [15]. Based on their theoretical analysis they predicted that the water elimination from the EG molecule ($EG \rightarrow C_2H_4O + H_2O$) also has the lowest energy barrier and is about 3.7 kcal·mol⁻¹ higher than that of ethanol. The decomposition of ethanol forms ethane in the H₂O elimination path ($C_2H_5OH \rightarrow C_2H_4 + H_2O$) whereas EG would form C₂H₄O ($EG \rightarrow C_2H_4O + H_2O$). Unlike ethanol, where the ethenol formation through H₂ elimination ($C_2H_5OH \rightarrow CH_2CHOH + H_2$) has a much higher energy barrier (106.3 kcal·mol⁻¹) [14], EG ($EG \rightarrow CH_2CHOH + H_2O$) in comparison only has a 70.3 kcal·mol⁻¹ barrier. Among C₂H₄O isomers either acetaldehyde or ethenol or both can be formed. Ye and coworkers [15] predicted the energy difference between enol (ethenol) and aldehyde (acetaldehyde) formation to be only 0.9 kcal·mol⁻¹ and thereby the possibility of both reaction routes ($EG \rightarrow CH_2CHOH/CH_3CHO + H_2O$), with enol as the more favored route. Thus, EG studies with respect to major decomposition product C₂H₄O differ from ethanol. Though acetaldehyde is part of most reaction mechanisms, the presence of ethenol is often restricted. Since ethenol is a direct decomposition product of EG we believe in its crucial importance.

The role of ethenol itself in the combustion chemistry is discussed since its first detection in hydrocarbon flames by photoionization mass spectrometry using synchrotron radiation [16]. Since most of the *in situ* mass spectrometry experiments performed in

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