

Pentanol: A Promising Fuel and Petrochemical Building Block

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Introduction

The increasing worldwide energy demand and the major environmental constraints on greenhouse gas emissions are strongly driving the search for alternative fuel and base chemical resources. Many studies have reported industrial, experimental and theoretical results on feedstocks derived from non-fossil processes, among which urban waste and biological feedstocks are the most promising. Biofuels produced from biomass show strong potential for reducing harmful emissions and alleviating petroleum shortages, making research in this area very attractive¹⁻⁴. Primary alcohols have already been considered for decades as sustainable fuel. Ethanol, belonging to the first generation biofuels, is widely spread as substitute for conventional diesel. Other alcohols such as propanol and *n*- and iso-butanol gained significant interest in the past for their higher energy density, higher cetane numbers and lower hygroscopic properties. To increase the energy content even more, the second generation biofuel *n*-pentanol is now extensively studied. *n*-Pentanol is a promising candidate for diesel blends not only due to its higher heating value, but also due to its low autoignition temperature and higher reactivity⁴⁻⁶. Furthermore, it is much easier to blend *n*-pentanol into conventional hydrocarbon fuels due to its longer carbon chain. Its performance in engines has been studied to minimize the CO, hydrocarbon, NO_x, and smoke emission,^{7,8} particulate emissions,⁹ mixing characteristics,¹⁰ and optimize the cetane number¹¹ of a pentanol/diesel blend. Experimental and modeling work on the combustion properties such as laminar flame speeds^{12,13} and ignition characteristics¹⁴ have been reported. In this work, the pyrolysis and combustion chemistry of *n*-pentanol is studied in two-fold. First, an experimental dataset was obtained on a Bench Scale set-up. Second, a kinetic model was constructed using the automatic kinetic model generation tool Genesys enabling a comparison between experimental and simulation results.

Experimental and simulation method

Experiment

The pyrolysis of *n*-pentanol has been studied experimentally on a Bench Scale set-up, which has been described previously by Djokic et al.¹⁵ and Harper et al.¹⁶. The reactor is an Incoloy 800HT tube of 1.475 m long with an internal diameter of 6 mm, placed in a vertical furnace consisting of four heating sections controlled by four thermocouples inside the reactor tube. The pressure is measured at the in- and outlet of the reactor, with a set point of 0.17 MPa. The pressure drop along the reactor can be neglected. Two sets of experiments were done, one with at a pentanol dilution of 1:4 in nitrogen gas, another one with a dilution of 1:1. For the first set, the pentanol inlet flow amounts up to 48 g h⁻¹, while for the second one it is equal to 120 g h⁻¹. The temperature inside the reactor was varied between 913 and 1073 K with increments of 20 K, in order to cover a wide conversion range. The reactor effluent was analyzed using two single GC's and one GC×GC, which allows on-line qualification and quantification of the complete product spectrum, using a time of flight mass spectrometer and a flame

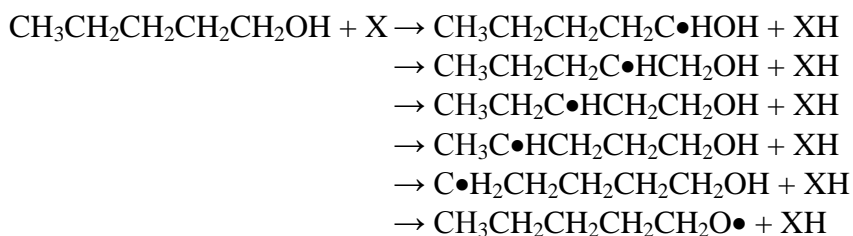
ionization detector respectively.

Kinetic model

A fundamental part of the computer simulations for chemical processes is the availability of a chemical kinetic model, i.e. a set of rate expressions of the occurring reactions. For the pyrolysis of n-pentanol, a kinetic model was constructed using Genesys¹⁷, an automatic kinetic model generator recently developed at the Laboratory for Chemical Technology (LCT). Genesys is integrated with advanced open-source chemo-informatics libraries, allowing the generation of kinetic models independent of the reactants, elements, or chemistry. Furthermore, Genesys makes use of a rule-based termination criterion. Reaction families relevant for hydrocarbon and oxygenates pyrolysis have been constructed, consisting of hydrogen abstraction reactions, β -scission reactions and the reverse radical addition reactions, homolytic bond scissions and the reverse recombination reactions, and CO formation reactions. Each reaction family is constrained to only allow relevant reactions to be generated. These constraints are defined based on the immediate surroundings of reactive centers, e.g. valency or hybridization, as well as on the molecule in its entirety, such as molecule size, presence of rings or aromaticity.

Kinetic models for thermal decomposition, steam cracking, and combustion processes can contain up to thousands of reactions, for which most of the rate coefficients have never been measured experimentally. Hence, estimation methods are necessary in order to bridge the data gap. In the kinetic model for the pyrolysis of n-pentanol, constructed with Genesys, most kinetic and thermodynamic parameters are estimated using group contribution methods. Furthermore, the n-pentanol pyrolysis sub-model generated by Genesys is merged with the Aramcomech¹⁸ base mechanism, which describes the pyrolysis and oxidation chemistry of small compounds, with up to 4 carbon atoms. The kinetics for the homolytic scission reactions of C-H, C-C, C-O and O-H bonds are taken from the literature, as well as the H₂O elimination in n-pentanol.¹⁹

Although estimation methods are the main fallback in the case of data shortage, their accuracy beyond the training set with which they were developed is questionable. Therefore, with the growing computational power and availability of high-performance computing solutions, many rate coefficients are nowadays calculated ab initio. In this work, the kinetics of the reactions for n-pentanol radicals have been determined from in-house ab initio calculations. During the pyrolysis of n-pentanol the first radicals appear when the C-C, C-O, C-H, or O-H bonds break. While unimolecular dissociation of the fuel molecule continues to be an important process as long as the fuel is still present in significant concentrations, abstraction reactions mostly by X = H, CH₃, OH radicals are driving the secondary chemistry. These abstraction reactions yield six different pentanol radicals, which will be denoted in the following as α -R, β -R, γ -R, δ -R, ε -R, and o-R, alluding to the location of the radical site.



The kinetic model generated with Genesys has been used in a reactor model to simulate the experimental data. The Bench Scale set-up can be modelled as an ideal plug-flow reactor¹⁶. Chemkin²⁰ is used as kinetic model simulation tool. The reactor conditions and inlet flow rates are taken from the experimental measurements. The temperature profile and pressure are imposed on the reactor.

Results and Discussion

The experimental and simulation results are given in Figure 1 and Figure 2 for the major and minor compounds respectively. Simulations have also been done with three models found in the literature by Heufer et al.¹⁹, Togbé et al.²¹ and Wang et al.²². Compared to the other models, the current work gives the closest agreement of the conversion with the experimental data. The predictions of the three main products, ethene, methane and CO, as a function of conversion is comparable to the experiments for the four models. Propene and ethane both exhibit a maximum in their mass fraction profile at a conversion of 90%. The simulations are able to capture the maximum, but it lies at a higher conversion. The model of Heufer et al. leads to the best propene simulations, although the differences are small between the models. For ethane, Togbé et al. shows a better agreement with the experimental data, as the models of Heufer et al. and Wang et al. are not able to capture the trend of the selectivity towards ethane as a function of the conversion. The water yields are similar for the four models, and the current work gives the best butadiene predictions, although secondary reaction pathways of butadiene are probably missing, which explains the overprediction only at high temperatures. Although the relative deviations of the simulations on these compounds are higher compared to the major products, the absolute deviations are of a similar order of magnitude.

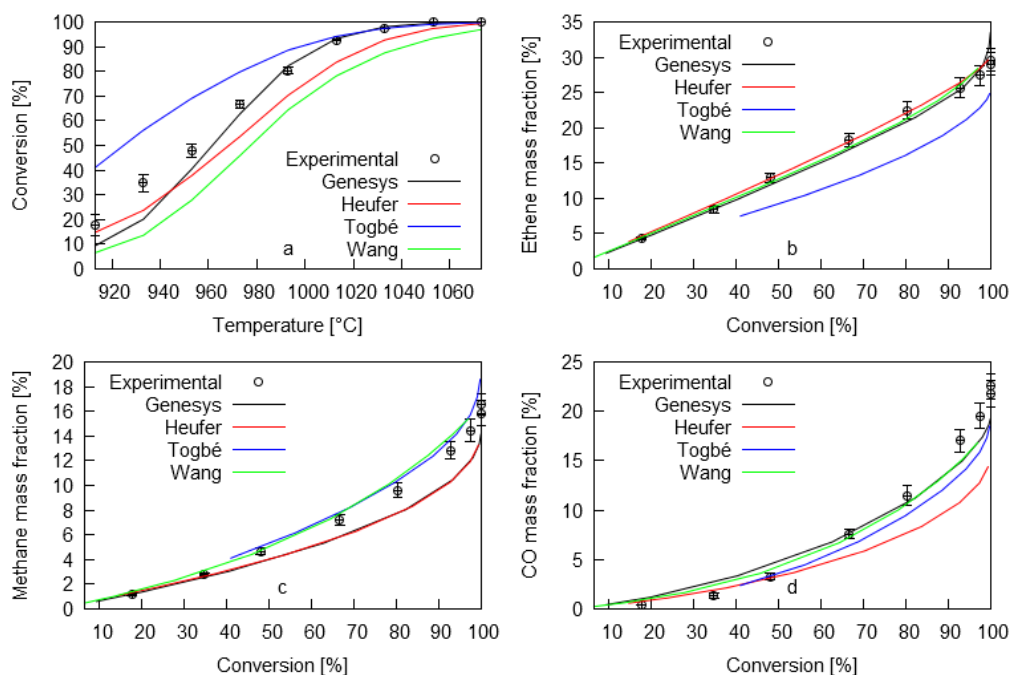


Figure 1. Experimental results (dots) and simulations (lines) for (a) the conversion of pentanol as a function of temperature, (b) the mass fraction of ethene as function of the conversion, (c) the mass fraction of methane as a function of conversion and (c) the mass fraction of CO as a function of conversion. The model generated by Genesys is compared to the models of Heufer et al.¹⁹, Togbé et al.²¹, and Wang et al.²².

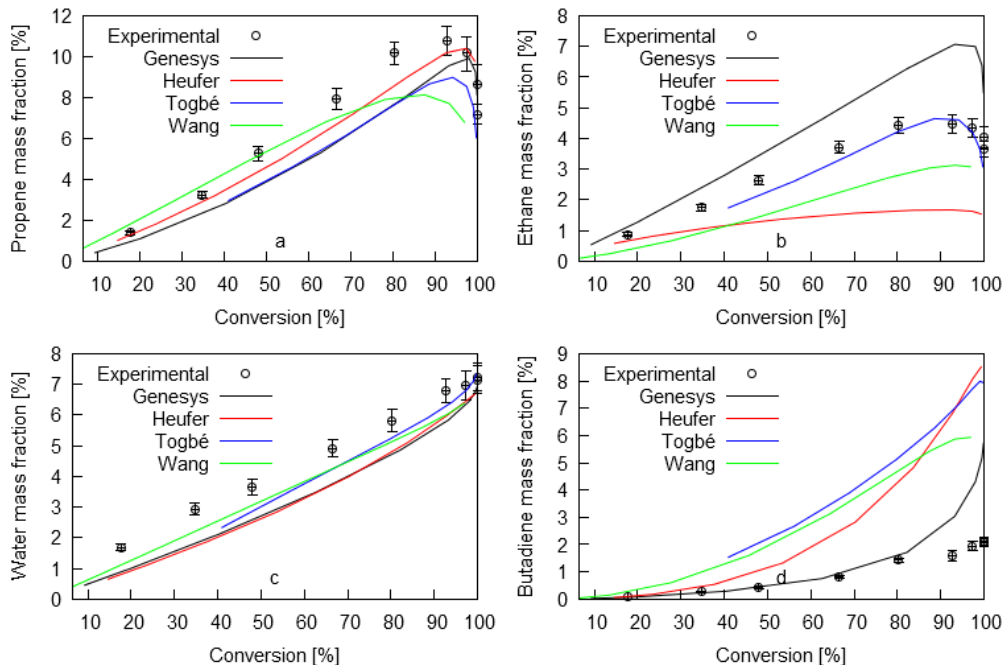


Figure 2. Experimental results (dots) and simulations (lines) for (a) the mass fraction of propylene, (b) the mass fraction of ethane, (c) the mass fraction of water and (c) the mass fraction of butadiene as a function of conversion. The model generated by Genesys is compared to the models of Heufer et al.¹⁹, Togbé et al.²¹, and Wang et al.²².

From the reactor simulations, the main decomposition pathways can be identified and their relative importance can be quantified. The initial decomposition of the n-pentanol radical happens through either a C-C bond cleavage or the direct elimination of a water molecule, forming pentene. Homolytic scission of C-O, C-H and O-H bonds do not play an important role. The weakest bond is, in agreement to studies of pentanol^{19,23} or other alcohols^{24,25}, the bond in β -position of the hydroxyl group, followed by the terminal C-C bond. Once a radical pool is created, these scission reactions decrease very rapidly in importance, and the main decomposition route is hydrogen abstractions, as shown in Figure 3.

The reaction scheme is recorded at the highest n-pentanol decomposition rate, which is at a distance of 37 cm into the reactor for the simulation at 973 K. At 37 cm, the set point temperature is already reached. The percentages indicate the relative rate of production compared to the total decomposition rate of n-pentanol. For the sake of clarity, no intramolecular hydrogen abstractions and well-skipping reactions have been added to the figure. Two intramolecular hydrogen abstraction reactions have a contribution of more than 1% compared to the total conversion rate of n-pentanol: the net conversion of δ -R to o-R amounts 2%, and the total net conversion of ε -R to α -R is around 1%. Also, one well-skipping reaction has a noteworthy contribution: o-R reacts to propene and the $\text{CH}_2\bullet\text{CH}_2\text{OH}$ with a production rate of 3%.

Around half of the o-R first undergoes a C-C- β -scission to formaldehyde and n-butyl. The remainder of the o-R decomposes through the well-skipping reaction mentioned above, while the α -R decomposes to n-propyl and vinyl alcohol. The β -R reacts via a C-O- β -scission, forming 1-pentene and a hydroxyl radical. The C-C- β -scission is also somewhat important, leading to ethyl and 1-buten-3-ol.

Two C-C- β -scissions are possible in γ -R, forming methyl and 1-buten-4-ol, and 1-butene and C•H₂OH, respectively. As already mentioned, δ -R is consumed by an intramolecular hydrogen abstraction reaction to α -R. Furthermore, it decomposes through two pathways: the formation of propene and C•H₂CH₂OH and a well-skipping reaction to formaldehyde and n-butyl, accountable for almost 10% of the total decomposition of n-propanol.

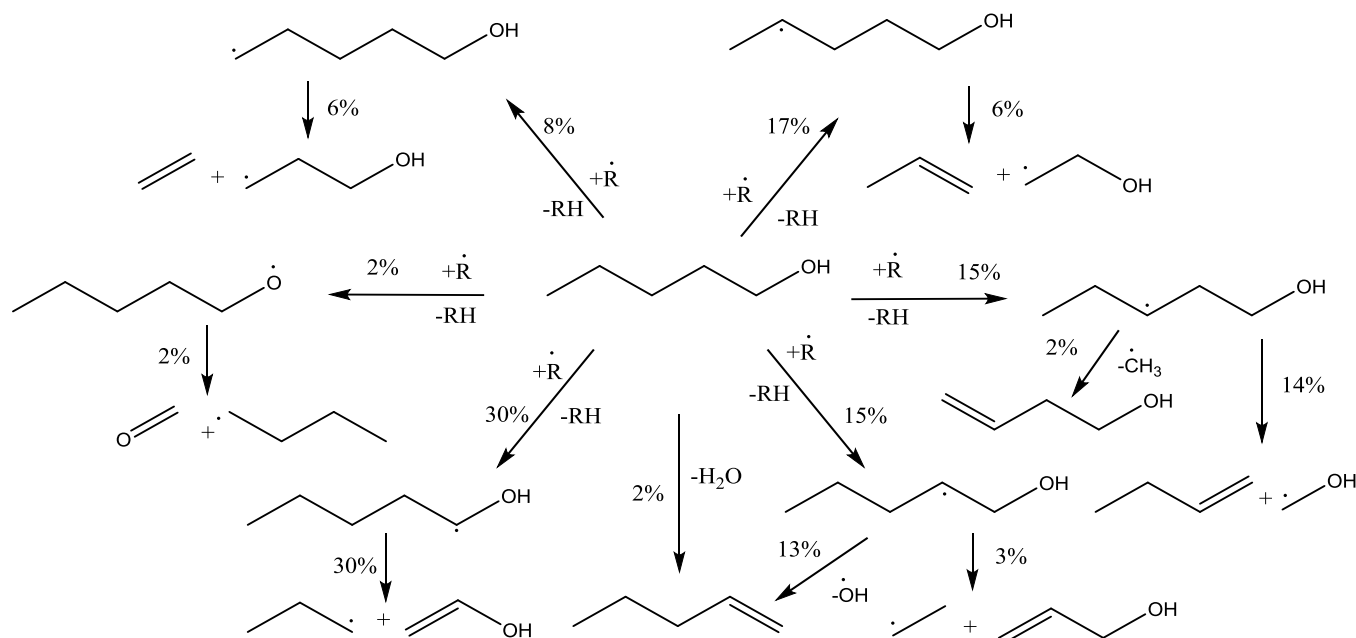


Figure 3. Initial decomposition of n-pentanol at a position of 37 cm in the Bench Scale set-up at 973 K. The percentages are the relative rates to the total rate of consumption of n-pentanol.

Conclusions

In view of the increasing worldwide energy demand and the major environmental constraints on greenhouse gas emissions, n-pentanol can be considered as a promising alternative fuel candidate. In this work, the pyrolysis and combustion chemistry of n-pentanol was studied in two-fold. First, the decomposition of n-pentanol has been performed in a flow reactor at various temperatures covering a wide conversion range. Second, in order to simulate the experimental data, a kinetic model was developed making use of the automatic kinetic model builder Genesys. For assignment of thermodynamic and kinetic parameters, data from literature and values estimated by group contribution methods were combined with newly calculated rate coefficients for reactions of the n-pentanol radical.

The product fractions of simulations and experiments are compared and a satisfactory agreement is achieved. The kinetic model developed by Genesys succeeds in describing both the conversion and selectivities of the main products. Rate-of-production analysis allows to identify the important reaction pathways and intermediates under pyrolysis conditions. The initiation reactions are homolytic scissions of C-C and the C-O bond, forming an initial pool of radicals. The C-C bond in β -position of the alcohol group is the weakest and has the highest contribution to the initial

decomposition. Once radicals are created, chain reactions mainly consisting of hydrogen abstraction reactions and β -scission reactions follow each other to form small olefins and oxygenates.

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