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# Kinetic model for reactions of indole under supercritical water gasification conditions

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## HIGHLIGHTS

- Simplifed network of indole SCWG.
- Detailed kinetic modelling of indole SCW.
- Reaction rate analysis of the model.

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## ABSTRACT

We developed a quantitative kinetics model for the homogeneous decomposition and gasification of indole in supercritical water at 550–650 °C based on a reaction network with 17 separate reaction pathways. The model accurately describes the effects of time, temperature, and initial concentrations on the concentrations of intermediate products such as aniline, toluene, and benzene as well as the terminal gaseous products such as $H_2$, $CH_4$, and $CO_2$. Modeling revealed that three steps are most important for $H_2$ production. Ring-opening of indole to form aniline is the fastest such step during the first few minutes at 600 °C, depletion of the large variety of gasifiable products dominates at times between 5 and 55 min, and water gas shift is the main $H_2$-producing reaction at longer times. The model also revealed that some of the potential pathways were kinetically insignificant at 600 °C. Such paths included methanation, gasification of benzene, steam reforming of indole, and formation of CO, $CO_2$, and $C_2H_6$ from intermediate products.



## 1. Introduction

Supercritical water gasification (SCWG) is a technology that is well suited to produce $H_2$ or $CH_4$ from organic material with high moisture content. Biomass, both terrestrial and aquatic, is such a material, and it has received significant attention [1–3]. SCWG processing conditions exceed the thermodynamic critical point of water ($T_c$ = 374 °C, $P_c$ = 22.1 MPa), and the combined action of thermal energy and hydrolysis breaks down the biomacromolecules into $H_2$, CO, $CO_2$, $CH_4$ and other products [4].

Model compounds have frequently been examined to learn more about the reaction chemistry occurring during SCWG. Chemical details are difficult to discern when working with real biomass, as the complexity of the feedstock often obscures the fundamental processes occurring. Some of these model compounds mimic structures in the biomass components of interest whereas others represent important intermediates identified in experiments with actual biomass. Indole is a model compound of this second type. It is a nitrogen-containing heterocyclic compound that likely forms from proteins during SCWG of protein-containing biomass such as algae [5]. Indole, once formed, is difficult to gasify [6]. We recently reported a detailed and systematic study on the gasification of indole in supercritical water [6] in quartz tubes. This report included a detailed reaction network with plausible reaction paths for the formation of the multitude of liquid- and gas-phase products detected during this uncatalyzed hydrothermal reaction.

This present report complements the prior experimental work by providing a quantitative kinetics model based on the indole SCWG network. Knowledge of the reaction kinetics is important for technological applications and for reactor design. It can also give insights into the relative importance of the different paths in the reaction network. Most previous SCWG kinetics studies dealt solely with production of gases and/or conversion of the feedstock

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[7–11]. These kinetic models did not describe the rates of (or often even identify) the reaction pathways that interconnect the various intermediate products.

Goodwin and Rorrer [12], however, developed kinetic models describing SCWG of xylose that accounted for the formation of intermediate products and gases. Very recently, Huelsman and Savage reported a detailed kinetics model for phenol SCWG that accounted explicitly for several of the intermediate products such as benzene and dibenzofuran [13], along with the gaseous products. Other than these two accounts, the SCWG literature does not contain any quantitative kinetics models that include specific intermediate molecular products. We note, however, that others are working on such models for the related system of SCW partial oxidation [14]. Regardless, these previous accounts deal with molecules containing only C, H, and O atoms. To the best of our knowledge, the literature contains no reports of reaction network models for the gasification of a N-containing compound in supercritical water. Such compounds are important intermediates from hydrothermal treatment of protein-containing biomass.

This article presents a quantitative kinetics model for indole SCWG that describes the concentrations of several liquid-phase products along with all of the important gaseous products. We use the experimental data and reaction network reported previously for the noncatalytic hydrothermal decomposition of indole [6]. After demonstrating that the model is consistent with the experimental results, we show that it can predict the influence of both water molar density and the initial indole concentration on the product concentrations. This present report on indole SCWG, along with our earlier article on phenol SCWG [9,13], provides the foundation of a modeling framework that can be useful for SCWG of other compounds, and eventually of whole biomass.

## 2. Model development

The model is based on the reaction network for indole SCWG deduced in our previous work [6]. That detailed network illustrated the pathways to all of the various intermediate products that had been detected, including those present in low yields. In this article, our interest is focused on developing a mathematical description of this reactive process that captures the behavior of indole, the major liquid-phase reaction products (toluene, aniline, and benzene), and the gaseous products. Accordingly, we have simplified the reaction network by lumping together several minor species and combining some sequential paths into single overall pathways. This lumping and combining reduces the number of pathways and thus the number of parameters in the corresponding model. The simplified network appears in Fig. 1. Indole reacts to form toluene, aniline, and benzene as the major liquid-phase products. All other liquid-phase products, which individually are in much lower concentrations, are lumped together and denoted as gasifiable products (GP). Gases may be formed by steam reforming of indole and by decomposition of the gasifiable products. In addition, the intermediate products can form stable products (SP) such as polycyclic aromatics. Finally, the network includes the water gas shift reaction and ammonia decomposition as potential pathways.

Having introduced the reaction network, we next describe in more detail each reaction path. The first five paths, shown below, involve reactions of aromatic molecules. We used balanced chemical reactions for each of these pathways.

$$\text{Indole } (C_8H_7N) + 2H_2O \xrightarrow{k_1} \text{Aniline } (C_6H_7N) + 2CO + 2H_2 \quad (R1)$$

$$\text{Aniline } (C_6H_7N) + H_2 \xrightarrow{k_2} \text{Benzene } (C_6H_6) + NH_3 \quad (R2)$$

$$\text{Indole } (C_8H_7N) + 2H_2O \xrightarrow{k_3} \text{Toluene } (C_7H_8) + NH_3 + CO_2 \quad (R3)$$

$$\text{Toluene } (C_7H_8) + H_2 \xrightarrow{k_4} \text{Benzene } (C_6H_6) + CH_4 \quad (R4)$$

$$\text{Indole } (C_8H_7N) + 4H_2 \xrightarrow{k_5} \text{Benzene } (C_6H_6) + NH_3 + C_2H_6 \quad (R5)$$

Reactions (1) and (3)show indole being attacked by water molecules to engender pyrrolic ring opening and form aniline and toluene, the two most abundant liquid-phase products. Aniline and toluene then undergo hydrogenolytic deamination and demethylation, respectively, to form benzene. We include hydrogenolytic pyrrolic ring opening in step 5 in the model because it may be an important source of $C_2H_6$, which was present in trace amounts among the gaseous products.

We lump together all of the other, less abundant, liquid-phase products into a pseudo-component we term gasifiable products (GP). Our previous experimental study revealed the presence of a large variety of different nitrogen-containing compounds, and one can reasonably expect these to be formed primarily from indole (step 7). We also include a path from benzene (step 6) to gasifiable products for completeness although we expect this path

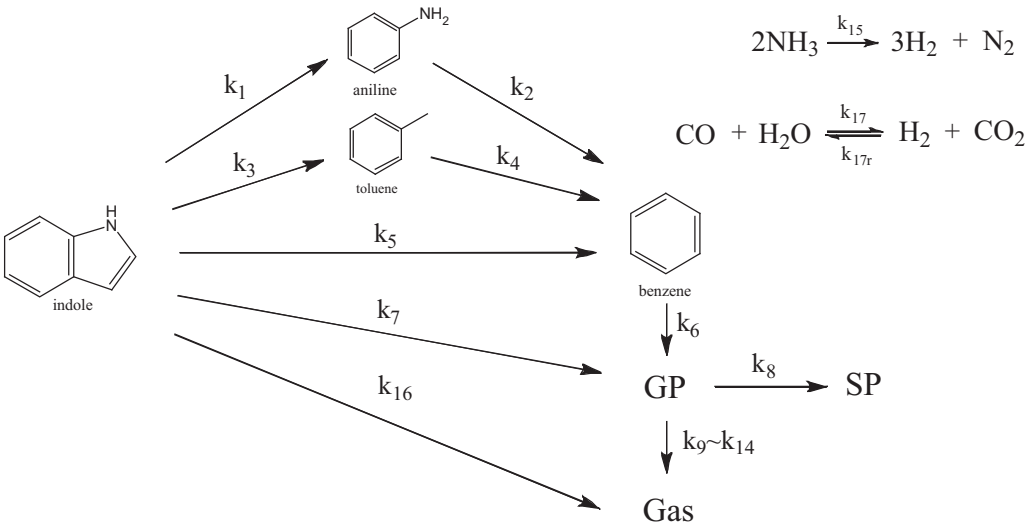


**Fig. 1.** Simplified reaction network for indole in supercritical water.