



Full Length Article

Isotope tracing study on hydrogen donating capability of supercritical water assisted by formic acid to upgrade heavy oil: Computer simulation vs. experiment



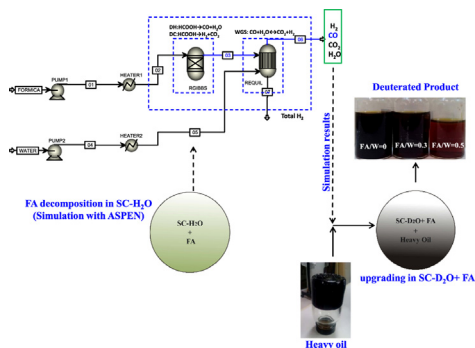
Morteza Hosseinpour^{a,b}, Shohreh Fatemi^{a,*}, Seyed Javad Ahmadi^a, Yoshito Oshima^b, Masato Morimoto^c, Makoto Akizuki^b

^a School of Chemical Engineering, College of Engineering, University of Tehran, P.O. Box: 11365-4563, Tehran, Iran

^b Department of Environment Systems, Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8563, Japan

^c Research Institute of Energy Frontier, National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba 305-8569, Japan

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Heavy oil upgrading
Thermodynamic simulation
LK-Plöcker EoS
Isotope labeling technique
Supercritical water

ABSTRACT

Due to the increasing attention of the experts working in refineries on innovative techniques for heavy oil upgrading, the current research is focused on in-situ upgrading of heavy oil in supercritical water (SCW) assisted by formic acid. In dry condition, formic acid (FA) decomposes by two parallel paths, namely decarboxylation ($\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2$) and dehydration ($\text{HCOOH} \rightarrow \text{CO} + \text{H}_2\text{O}$) to produce hydrogen and carbon monoxide, respectively. Water-gas shift (WGS) reaction which is taken place by SCW and carbon monoxide provides active hydrogen (AH) as a more favorable hydrogen source for upgrading heavy oil in SC condition. In the current study, first, thermodynamic simulation of FA decomposition in SCW was studied to evaluate the contribution of hydrogen from water in Aspen suite environment by performing sensitivity analysis. Here, the effects of operational parameters (temperature, pressure, FA to water ratio) were studied on the above-mentioned reaction. The simulation results as well as experimental data show that the increase of FA to water ratio (FA/W) enhances the contribution of dehydration path, which means that SC works better as a precursor of hydrogen due to the higher concentrations of CO at SC condition. In order to specify the portion of hydrogen from WGS and decarboxylation reaction, the isotope labeling technique was applied by replacing ordinary water (H_2O) with heavy water (D_2O) in SC condition in the presence of heavy oil and FA. After combining the experimental data and Hansen solubility parameter of water (δ_{H_1}), it was revealed that temperature has dual effects which can influence on coking reaction by physical and chemical reaction. It means that an increasing in temperature can suppress

* Corresponding author.

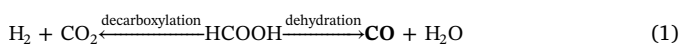
E-mail address: shfatemi@ut.ac.ir (S. Fatemi).

the coke formation due to better miscibility of oil with water, while at an extreme temperature condition (500 °C), the dominant condensations of polycyclic aromatics are conspicuous; consequently the rate of coking is enhanced. High pressures (~45 MPa) also lead to the more coking reaction through the influence on the phase behavior of oil-water (δ_H and AH%) in which asphaltene conversion path is converted to coke rather than light products. Accordingly, $T = 450$ °C and $P_w = 27$ MPa were proposed respectively as an appropriate temperature and pressure for heavy oil upgrading in supercritical water assisted by FA to cause less coke and produce more light liquid products.

1. Introduction

Although there are serious challenges for refineries to deal with unconventional heavy oil which contains a large amount of precursor of carbon residue and heteroatoms, the demand for such oil increases because of the following three reasons: (1) heavy oil and bitumen resources are worldwide assets, approximately 6 trillion barrels, (2) the demands for low sulfur light oil increase incessantly, because of environmental rigid regulation, and (3) the light crude oil reserves are exhaustible which the H/C ratio of oil fields are reduced [1].

Upgrading heavy oil and residua in the presence of hydrogen-donor is an innovative environmentally friendly approach, which has recently attracted considerable attention [2–4]. From an industrial point of view, heavy oil upgrading can proceed via carbon rejection and hydrogen addition processes aiming to increase the hydrogen to carbon ratio (H/C) [5]. Carbon rejections, as thermal processes, are simple than hydrogen addition processes, albeit with the low yield of liquid product, which is not preferred by refineries experts. Furthermore, due to considerable amount of impurities as side products as well as low quality of upgraded product, applying hydrogen and catalyst is more suitable for purification to meet the standards and environmental regulations of market demands [6]. For such heavy oil hydro-treatment, the required external hydrogen supplies from steam reforming of natural gas, known as an expensive process, is indispensable [7]. Regardless of economic and safety aspects in production, transportation, storage and usage of produced hydrogen by this method, reforming unit produces a significant amount of carbon dioxide as a by-product which is hazardous to the environment [8]. As a consequence, much attention has been paid to replace external hydrogen with in-situ hydrogen-donors as alternative for heavy oil upgrading. Among the various sources of hydrogen-donors, formic acid (HCOOH, FA) can be a worthy candidate for production of in-situ hydrogen. FA in liquid state at room temperature is a non-toxic compound and has high energy density [9]. Further, it can be transported easily without any safety precaution. It has two isomers, cis-HCOOH and trans-HCOOH, with two-hydrogen in one-side and opposite side respectively [10]. According to the literature, FA decomposes by molecular elimination mechanism in two parallel competitive paths, namely decarboxylation and dehydration [10]:



Also the theoretical and experimental studies show that decarboxylation path is the foremost avenue in decomposition of FA in the liquid phase (e.g. hydrothermal system) while in case decomposition in gas phase, dehydration path with one order of magnitude is dominant.

Recently, numerous attentions have been paid to the heavy oil upgrading in supercritical water (SCW) [1,11]. Due to variation in thermodynamic and transport properties of water near or above the critical point ($T_c = 374$ °C, $P_c = 22.1$ MPa), a modification in miscibility (solvation and dispersion effects) between SCW and heavy oil is expected to suppress coke formation significantly [12,13]. Also gases, which are dissolved completely in SCW, have a positive effect on kinetic and thermodynamic of reaction medium [14]. For instance, the previous investigation on hydrogenation via partial oxidation of heavy oil [15,16] and model compounds [17–20] in the presence of SCW showed that hydrogen can be produced from water-gas shift reaction (WGSR): $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$. Regarding the solvation and dispersion effects

of SCW, this may lead to a reaction with them more effective than the external hydrogen with a significant influence on hydrogenation of hydrocarbon albeit with less coke.

Most probably, Sato et al., are the only researchers who have considered the effect of FA on heavy oil upgrading in SCW comprehensively [21]. Their study on decomposition of bitumen conducted in SCW + H₂, SCW + CO, toluene and tetralin, as H-donor, revealed that decomposition of asphaltene was promoted and coke formation was inhibited when SCW + HCOOH was used. In other similar research performed by same author in the semi-batch system [22], bitumen conversion in the presence of hydrogen and carbon dioxide in SCW (SCW + H₂ + CO) was accomplished. The increase in hydrogen to carbon ratio (H/C) of oil product eluted from the reactor and the hydrogenation of asphaltene as well as suppressed coke formation were attributed to the active hydrogen (AH) species through forward and reverse WGSR in SCW + H₂ + CO₂. The reason for more activity of AH (from water) than external molecular hydrogen may be due to the capability of existing near reactants (radicals) in supercritical water condition. In all of the studies mentioned above, however, there is no information about the part of AH contributed to the hydrogenation of heavy oil in SCW in the presence of FA.

Due to the significance of AH from WGSR vs. molecular hydrogen from decarboxylation paths, the present study focuses on heavy oil upgrading in the presence of SCW and FA as a hydrogen-donor. Accordingly, following two main steps was considered to elucidate the chemical role of SCW, as a source of AH by WGSR, during the heavy oil upgrading in the presence of FA:

- Due to the significance of AH in heavy oil upgrading, the contribution of this kind of hydrogen relative to total hydrogen should be estimated in various operating conditions. Since, SCW has a density between a liquid and gas, predicting the decomposition of FA in this medium via decarboxylation or dehydration is not a simple matter. A thermodynamic analysis in Aspen Plus software environment, which provides a powerful *sensitivity analysis* capability, is an appropriate strategy for this case [23]. However, due to the limitation of thermodynamic model, i.e., equation of state (EoS), for such a significantly high pressure and temperature condition, a suitable EoS should be considered in advance. By applying a proper EoS, thermodynamic simulation of FA decomposition in SCW could be started and the result can be verified by the experimental data.
- Hydrogen from water (or via WGSR) was detected by the isotope labeling technique where light water (H₂O) was replaced with heavy water (D₂O). Then, upgrading of heavy oil was accomplished in the presence of FA and D₂O under supercritical condition, dealing with two parallel competitive sources of hydrogen, i.e., hydrogen produced from water (AH) and molecular hydrogen from decarboxylation path (H₂). After hydrogenation of heavy oil in that condition, analysis of deuterated oil sample was done by ATR-IR technique which is able to distinguish two kinds of hydrogen sources by the difference in wavenumbers ($\nu_{\text{C-H}}$) of carbon-hydrogen (C–H) and carbon-deuterium (C–D) chemical bonds [24,25].

This paper provides important information about the role of AH from SCW during upgrading of heavy oil using all the results which include water contribution as a hydrogen-donor and mass distribution

Download English Version:

<https://daneshyari.com/en/article/6630989>

Download Persian Version:

<https://daneshyari.com/article/6630989>

[Daneshyari.com](https://daneshyari.com)