

Packed-bed microreactors for understanding of the dissolution kinetics and mechanisms of asphaltenes in xylenes



Chuntian Hu^a, Andrew Yen^b, Nikhil Joshi^c, Ryan L. Hartman^{d,*}

^a Department of Chemical and Biological Engineering, University of Alabama, Tuscaloosa, AL 35487, USA

^b Nalco Champion, An Ecolab Company, Sugar Land, TX 77478, USA

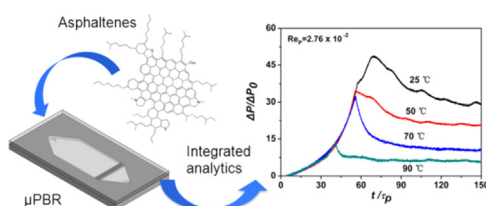
^c Anadarko Petroleum Corporation, The Woodlands, TX 77380, USA

^d Department of Chemical and Biomolecular Engineering, New York University, Brooklyn, NY 11201, USA

HIGHLIGHTS

- μ PBR was an excellent platform for studying asphaltenes dissolution in porous media.
- Longer shut-in time facilitated the removal of asphaltenes.
- At lower Re_p of 0.69×10^{-2} , more asphaltenes were removed.
- Asphaltenes deposited at higher *n*-heptane vol% were easier to dissolve.
- More asphaltenes were removed as temperature increasing from 25 to 90 °C.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 23 June 2015

Received in revised form

29 September 2015

Accepted 10 October 2015

Available online 21 October 2015

Keywords:

Asphaltenes

Dissolution

Porous media

Packed-bed microreactor

Deposition

ABSTRACT

Insightful information concerning the dissolution of asphaltenes in quartz porous media was acquired through the use of transparent packed-bed microreactors (μ PBRs), inline UV–vis spectroscopy and pressure transducers. Experimental results showed that longer shut-in time (16 h) facilitated the removal of asphaltenes, but the dissolution rate constants decreased gradually. At larger Re_p values of 5.52×10^{-2} , less time was allowed to dissolve asphaltenes and as a result less asphaltenes were removed. At a higher *n*-heptane volume composition of 80 vol%, more low molecular weight asphaltenes were deposited in μ PBRs but were easier to dissolve. At temperature range of 25–90 °C, more asphaltenes were removed as increasing temperature. Estimation of permeability–porosity relationships indicated that even when ~70–90 wt% asphaltenes were removed from the damaged packed-bed microreactors (D μ PBRs), the permeability impairments were still much lower than expected. The remaining asphaltenes in the D μ PBRs plugged the pore throat of porous media, and as a result resisted the flow of fluids. Understanding the dissolution kinetics and mechanisms of asphaltenes in porous media can be useful in designing remediation treatments that minimize production losses and the resultant economic losses.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Asphaltene science broadly impacts our everyday lives in such varied ways as manufacturing, transportation, roofing, and especially conventional and unconventional energy productions. Understanding

asphaltene science is of significant importance for designing remediation treatments that could minimize production losses and maximize economic interests. Asphaltene is defined operationally as *n*-heptane or *n*-pentane insoluble, toluene-soluble component of a given crude oil (Mullins et al., 2007). The fraction consists primarily of C, H, N, O and S, as well as trace amount of Fe, Ni, and V. The intrinsic properties such as molecular structure, color and chemical composition vary with many factors such as reservoir geography, pressure,

* Corresponding author.

E-mail address: ryan.hartman@nyu.edu (R.L. Hartman).

and temperature (Juyal et al., 2013). For example, asphaltenes precipitated from a given crude oil using *n*-heptane as a precipitant are usually dark-colored solids with specific gravity of ~ 1.2 , hydrogen to carbon atomic ratios of $\sim 1.2:1$, and molecular weight range of 500–1000 Da (Mullins et al., 2007). Even after decades of academic and industrial investigation, asphaltene-related research is still an important and difficult challenge due to their thermodynamic and functional complexities. Currently, understanding asphaltene structures (Bouhadda et al., 2007; Eyssautier et al., 2011; Mullins, 2010; Mullins et al., 2012; Sedghi et al., 2013), aggregation and solubility behaviors (Arteaga-Larios et al., 2005; Maqbool et al., 2011a; Murgich et al., 2002; Rogel, 2000; Sedghi et al., 2013; Spiecker et al., 2003; Wiehe, 2012), precipitation (or flocculation) (Andersen and Stenby, 1996; Hu et al., 2015; Maqbool et al., 2011b; Peramanu et al., 2001), deposition (Buckley, 2012; Hoepfner et al., 2013; Hu and Hartman, 2014; Hu et al., 2014, 2015; Juyal et al., 2013), and dissolution (Carbognani, 2001; Kaminski et al., 2000; Permsukarome et al., 1997), all remain essential research topics in this area.

Asphaltenes precipitation and deposition can occur during the production, transportation and refinery process of a given crude oil. Crude oil is a very complex chemical mixture that containing thousands of different kinds of components, and asphaltenes are the heaviest and most problematic fractions. Many factors, such as changes in pressure, temperature and bulk fluid composition, can cause asphaltenes to precipitate, and then deposit onto a solid surface, thus plug the reservoir porous media, transportation pipelines, and refinery equipments (Buckley, 2012; Chang and Fogler, 1994a,b; Hoepfner et al., 2013; Kaminski et al., 2000; Maqbool et al., 2011a,b; Mullins, 2010; Wang et al., 2004; Wattana et al., 2005). This decreases the oil production and increases the operation cost. In porous media, two recognized models were proposed: surface adsorption and mechanical entrapment (e.g., hydrodynamic bridging/pore throat plugging) (Almehaideb, 2004). Surface adsorption is reversible with asphaltenes desorbing from solid surfaces as the bulk concentration decreases. Mechanical entrapment is a physical pore throat blocking process by precipitated asphaltene particles. Research results show that both of these two mechanisms exist and mechanical entrapment dominates the deposition process in the porous media (Hu and Hartman, 2014; Hu et al., 2014, 2015).

Asphaltenes removal has attracted more attention from scientists and engineers (Carbognani, 2001; Kaminski et al., 2000; Permsukarome et al., 1997; Zhang et al., 2003), both from industry and academia, with the increasing trend towards the exploitation of heavier crude oil and the application of secondary and tertiary methods in oil recovery (Permsukarome et al., 1997). Various operational techniques (e.g., squeeze treatments and mechanical pigging) have been used to remediate near-wellbore damage. Squeeze treatments usually involve the use of aromatic-based solvents, such as toluene and xylenes, to dissolve asphaltene deposits. Successfully orchestrating a squeeze treatment to remove asphaltenes requires a detailed understanding of fluid placement and the dissolution mechanisms, which ultimately depend on the formation damage mechanism (Hu and Hartman, 2014; Hu et al., 2015).

Xylenes are aromatic hydrocarbon mixture of molecules consisting of a benzene ring with two methyl groups at various substituted positions (i.e., ortho-xylene, meta-xylene, and para-xylene), and they are usually produced by the methylation of toluene and benzene. In oil industry, xylenes are widely used to solve crude oil wax and asphaltene problems in pipelines due to the fact that wax and asphaltenes are highly soluble in xylenes (Bailey and Allenson, 2009).

Microchemical systems, taking advantages of reduced heat and mass transfer limitations, enhanced mixing, and high surface-area-to-volume ratios (Günther and Jensen, 2006; Hartman, 2012; Hartman and Jensen, 2009; Hartman et al., 2010a,b, 2009; Hessel

et al., 2005; Hu and Hartman, 2014; Hu et al., 2013, 2014, 2015; Jensen, 2001, 2006; Kreutzer et al., 2008; Losey et al., 2001; Marre et al., 2008; Sahoo et al., 2007; Trachsel et al., 2005; Yen et al., 2005), serve as ideal tools to investigate multiphase flows and reactions in porous media. Low Reynolds number laminar flows are generally obtained in the microchemical systems due to their reduced length scales (Jensen, 2001), and mixing of multiphase flows have been shown to achieve in microseconds (Günther and Jensen, 2006; Hatakeyama et al., 2006; Song et al., 2003; Zheng and Ismagilov, 2005). Lab-on-chip designs are capable of operating at high pressures (e.g., >2500 psi) and temperatures (e.g., >350 °C). Silicon (Jensen, 2001) and glasses (Chow, 2002; Kikutani et al., 2002) are two widely used materials that were chosen depending on the experimental conditions (e.g., temperature, pressure) and the availability of fabrication process. The design of microchemical systems with online analytics creates the potential to advance the understanding of asphaltene science at characteristic length scales.

In the present work, transparent packed-bed microreactors (μ PBRs) with inline UV–vis spectroscopy and pressure transducers were used to investigate the dissolution of asphaltenes in porous media. They provide an excellent platform to bridge the knowledge gap between macro-scale (i.e., oilfield chemistry) and molecular level events. Four factors, shut-in time (0–16 h), Reynolds number ($0.69\text{--}5.52 \times 10^{-2}$), *n*-heptane volume composition (50–80 vol%), and temperature (25–90 °C), were investigated, and the dissolution kinetics and mechanisms were discussed. Our experimental results could be helpful in designing remediation treatments that minimize production losses and the resultant economic losses.

2. Materials and methods

2.1. Materials and instruments

Toluene (HPLC grade), ethanol (absolute), *n*-heptane (HPLC grade), and xylenes (mixed, >97%) were obtained from Alfa Aesar. Quartz sand (30–40 mesh) was purchased from VWR International. The asphaltenes used in the present study were prepared from a Wyoming field deposit, and the preparation process was discussed in the previous works (Hu and Hartman, 2014; Hu et al., 2014, 2015; Juyal et al., 2013). All liquids were used without further purification.

UV–vis spectroscopy and high-pressure syringe pumps (65 DM) were manufactured by Ocean Optics and Teledyne ISCO, respectively. Check valves, pressure reducing valves, and back pressure regulators were purchased from IDEX Health & Science. Pressure transducers (19C500PG4K) were purchased from Honeywell Sensing & Control. Ultrasonic bath and heated circulating water bath were acquired from VWR International.

2.2. Fabrication of μ PBRs

The transparent μ PBRs were fabricated from a 1.1 mm Pyrex wafer and a 1 mm polished single crystal silicon wafer. The fabrication process used to create the transparent μ PBRs primarily included (i) photolithography steps of spin-coating, exposure, and development, (ii) deep reactive ion etching (DRIE), (iii) cleaning, (iv) anodic bonding of the 1.1 mm Pyrex wafer to the single crystal silicon wafer, and (v) dicing into μ PBR chips (Hu and Hartman, 2014; Hu et al., 2014). Fig. 1a shows a photograph of the 45 μ L μ PBR with dimensions of 5.0 (length) \times 1.8 (width) \times 0.21 (thickness) cm³. The microchannel is 2.2 cm in length, 9 mm in width and 300 μ m in depth. Near the exit of the microchannel, there are 30 rows of pillars of 20 μ m in diameter which are spaced

Download English Version:

<https://daneshyari.com/en/article/154538>

Download Persian Version:

<https://daneshyari.com/article/154538>

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