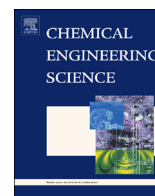




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# Characterization of pore coking in catalyst for thermal down-hole upgrading of heavy oil



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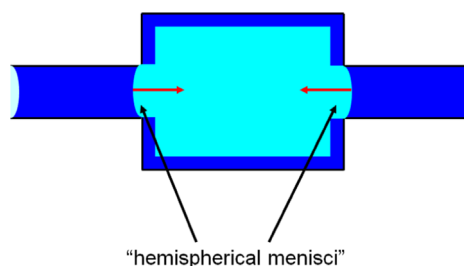
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## HIGHLIGHTS

- Novel experimental technique for studying coking.
- Method to understand spatial juxtaposition of coking pores.
- Assess impact of different process conditions on pore structure.
- Aid to design of deactivation-resistant catalysts.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Heavy oil and bitumen are a potential alternative energy source to conventional light crude. However, recovery of these resources can have substantial environmental impact. Downhole upgrading offers the prospect of both improving recovery, and decreasing environmental impact. However, use of catalysts to enhance downhole upgrading is limited by the need for one that can survive the extreme coking conditions arising from the cracking of heavy oil. In this work the potential of hydrogen donors to improve upgrading and enhance catalyst lifetime was considered. In order to extract detailed information on the catalyst structural evolution during reaction a novel parallel adsorption and thermoporometry characterization method was used. This technique allows detailed information to be obtained on the spatial juxtaposition of different pores, and their relative connectivity, as well as on size distributions. For catalyst operated at the conditions studied, it has been found that coking arises in smaller pores branching off the larger pores providing access to the catalyst interior. It has been found that while coking following use of different types of hydrogen donor leads to similar primary patterns of evolution in the pore-scale descriptors of the remaining accessible void-space, differences do arise in the overall accessible volume. Hence, it seems the hydrogen donor affects the location rather than general nature of the pore structure changes. However, at a secondary level of scrutiny, some differences in pore-scale evolution are also identified for different hydrogen donors. These differences identified helped the understanding of variations in the performance of different hydrogen donor and catalyst combinations.

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## 1. Introduction

Peak production of conventional light oil is likely to occur beyond 2035 (IEA, 2011). Thereafter there will be a decline in supply if alternative sources are not found and exploited. Heavy oil

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and bitumen represent a potential alternative to conventional oil. However, heavy oil and bitumen cannot be refined by conventional refineries without upgrading to convert them to synthetic light crude oil (Hart et al., 2013, 2014). Heavy oil and bitumen can be recovered using in-situ combustion. In-situ combustion methods involve burning part of the oil to recover the rest, by using the heat produced from the combustion reactions to reduce the viscosity of the remaining oil and allow it to flow to a producer well. One such method is the Toe-to-Heel Air Injection (THAI) method (Shah et al., 2010). In THAI, air is injected through a vertical injector well to supply the oxidant for a flame front which sweeps through the reservoir. The oil mobilized by the heat from the flame front flows down to a horizontal producer well towards the base of the reservoir. Very high temperatures, up to 600–700 °C can be obtained in the reservoir. Hence, the oil may undergo pyrolysis, and, also, upgrading reactions due to the natural catalytic activity of the host rock. The Catalytic upgrading Process In-situ (CAPRI) is a way to further enhance the upgrading arising from the THAI process itself. In CAPRI the horizontal producer well is wrapped around with an annular packed-bed of upgrading catalyst. As the mobilized heavy oil flows towards the producer well it passes through the packed bed of catalyst and undergoes further upgrading reactions. While the catalyst lifetime need only be of the order of a few days, which is the time for the flame front region to pass a particular location, the conditions the catalyst experiences are severe.

The reactions involving heavy oil taking place on the catalyst are highly likely to produce solid carbonaceous deposits, generally called 'coke'. This coke can smother active sites, and/or prevent access of reactants to the catalyst pellets completely by blocking of surface pores. The spatial distribution of coke depends upon the balance between the rates of reaction and mass transfer. A rapid coking reaction, relative to the rate of mass transport, is likely to lead to pore-mouth blocking, whereas a slower reaction is likely to lead to a more even distribution of coke. The rate of mass transfer is affected by the pore structure of the catalyst pellet.

Hart et al. (2013), successfully demonstrated that with better control of the oil flow, injected hydrogen can significantly improve the quality of the produced oil and reduce the coke build up on the surface of the catalysts. However due to the difficulties and expense of supplying gaseous hydrogen to the well, hydrogen donor solvents may be considered as an alternative. Cyclohexane and tetralin are widely used as hydrogen donor solvents for industrial applications such as nylon and coal liquefaction respectively. Dehydrogenation of cyclohexane for hydrogen storage and supply, as well as the use of tetralin as a donor solvent for coal/oil shale liquefaction and thermal/catalytic upgrading of heavy vacuum residues, have been extensively documented (Biniwale et al., 2005; Peden and Goodman, 1987; Liu and Fan, 2002; Alemán-Vázquez et al., 2012). In this study both of these solvents have been used as a potential source of continuous supply of hydrogen for the CAPRI catalyst to effect upgrading and as diluent for higher recovery.

The pore structures of catalysts are generally characterized using techniques such as gas adsorption. An additional technique, which is gaining popularity, is thermoporometry. However, these techniques have problems with pore-pore interaction phenomena affecting the accuracy of the pore size distributions for disordered solids that are particularly acute for coked catalysts (Gopinathan et al., 2013). However, these issues, which will be described in more detail below, can be overcome by the novel integrated method used in this paper (Shiko et al., 2012). In this work, rather than using gas sorption or thermoporometry separately, we will combine them into a composite technique. This new technique consists of performing thermoporometry studies using the adsorbate from an adsorption experiment as the probe fluid at different

levels of pellet saturation (with adsorbate). As will be seen below, this novel method delivers much more information on the relative proximity and connectivity of pores affected by coking or left open, and thereby gives a more detailed picture of the coking process. This more detailed picture of pore structure evolution during coking enables a better idea of how to make catalysts more resistant to coking to be obtained.

In this work, we will look at the potential benefits of using a guard bed of activated carbon to protect the catalyst from deactivation, and the impact of the use of various different hydrogen sources for improving upgrading on coking. In particular, the aim of this work is to study the effects of the combination of choice of hydrogen source and a particular catalyst pore structure has on coking resistance for that catalyst. This is to enable a more informed selection of hydrogen source for a given catalyst.

## 2. Theory

### 2.1. Gas sorption

Pore structural characterization by gas sorption is based on the phenomenon of capillary condensation. The Kelvin equation (Rouquerol et al., 1999) suggests that the logarithm of the relative pressure at which a vapour will condense within a pore is inversely proportional to the pore size:

$$\ln\left(\frac{P}{P_0}\right) = -\frac{k\gamma V_m \cos \theta}{RT(r_p)} \quad (1)$$

where  $P/P_0$  is the relative pressure at which condensation occurs in a cylindrical pore of radius  $r_p$ ,  $k$  is a geometry parameter and depends on the pore and meniscus geometry (for a cylindrical pore open at both ends  $k=1$ ; and for a pore with one dead end, or for adsorption from a hemi-spherical meniscus,  $k=2$ ),  $\gamma$  is the surface tension and  $V_m$  is the molar volume of the condensed liquid phase,  $\theta$  is the contact angle with which the liquid meets the wall, and  $T$  is the absolute temperature. Based on the Kelvin equation, the relative pressure needed to condense vapour in a through cylindrical pore, with a sleeve-shaped meniscus formed by the surface adsorbed layer, is the square root of the relative pressure needed to condense vapour starting from a hemi-spherical meniscus formed at the end of a dead-end cylindrical pore (Rouquerol et al., 1999). This sensitivity to meniscus geometry means there is not necessarily a monotonic relationship between the applied pressure and the characteristic size of pore in which condensation will have occurred for inter-connected, disordered solids.

In a through ink-bottle pore geometry, consisting of a large pore body sandwiched between two narrower necks, the presence of the larger body may be concealed by the 'advanced condensation effect', originally proposed by De Boer (1958). As illustrated in Fig. 1, condensation in the pore necks via a cylindrical sleeve-shaped meniscus will lead to the development of hemispherical menisci at the two entrances either end of the pore body. If the pressure for this neck-filling process exceeds that for filling of the pore body via a hemispherical meniscus, then the body will also fill simultaneously with the necks, and the two different pore sizes will appear as one. The physical occurrence of the advanced condensation effect has been observed experimentally using both integrated mercury porosimetry (Hitchcock et al., 2014) and magnetic resonance imaging methods (Hitchcock et al., 2010). The advanced adsorption effect, also known as the 'cascade effect', has also been seen in Monte-Carlo simulations of gas adsorption (Coasne et al., 2007).

The 'advanced condensation effect' (De Boer, 1958) is a particular problem when studying coking catalysts with gas sorption

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