

Now you see them, now you don't, now you might see them again! A review of the systematics of alkylphenol occurrence in conventional and heavy oil petroleum systems.

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Summary

Alkylphenols are small hydroxylated aromatic compounds that are ubiquitously present in conventional oils and gas condensates at concentrations up to hundreds, or even thousands, of ppm and are found at equilibrium in oil field waters in contact with phenol containing petroleums. They are known to display unique partition behavior within the crude oil / brine / rock phases in petroleum systems, having high vapor pressures, low oil/water partition coefficients and some affinity for solid sorption and these partition properties have been described under reservoir conditions. Alkylphenols can impact fluid rock interactions and reservoir system wettability and it has been shown that they can also change wettability if added to reservoir systems during fluid floods. Generated initially by alkylation and isomerisation reactions in source rocks during petroleum generation, they are removed from petroleum during long range petroleum secondary migration and by advanced levels of in reservoir biodegradation. They can however, be generated by thermal alteration of crude oil polar fractions, including asphaltenes at elevated temperatures. In this paper we review over 30 years of our work on the source rock and high temperature thermal origins, thermodynamics and partition behavior of phenols and also their kinetics of generation at high temperatures during thermal alteration of organic matter. We show how the charged oils to the L. Cretaceous oil sands reservoirs in Alberta, all likely originally contained alkylphenols when sourced, but that the long distances migrated and the heavy and severe biodegradation levels of the oils in the oil sands result in the oils being, now, low molecular weight (C_0 - C_3) phenol free! We also discuss how alkylphenols added to bitumen thermal recovery process fluid streams via injection, or generated during thermal recovery, can impact reservoir state or be used as quantitative tracers of reservoir phase and flow behavior.

Review and methods

Alkylphenols are small hydroxylated aromatic compounds, including the parent molecule phenol and with increasing addition of alkyl groups are known as cresols (C_1 alkylphenols) and xylenols (C_2 alkylphenols) that are ubiquitously present in conventional oils and gas condensates, at concentrations up to hundreds or even thousands of ppm. They can be quantitatively analysed to a high degree of accuracy and precision using solid phase extraction and gcms methods (Bennett et al., 1996; 2007). They are found at equilibrium concentrations in oil field and produced waters in contact with phenol containing petroleums (Dale et al, 1997a; Taylor et al, 1997) and their thermodynamic properties under reservoir conditions have been reported (Dale et al, 1997b). They have unique partition behavior between the solid, liquid and gaseous phases in petroleum systems(Taylor et al, 1997), having high vapor pressures, low oil/water partition coefficients(high water solubility) and some affinity for solid sorption and these partition properties have

been described under reservoir conditions using a novel equilibration system (Bennett et al, 1997; 2003). Alkylphenols can impact fluid rock interactions and reservoir system wettability (Bennett et al, 2007; 2010) and it has been shown that they can also change wettability if added to reservoir systems during fluid floods (Larter et al, 2000, 2007), potentially even generating oil wet, leaky seals (Aplin and Larter, 2005). We have shown previously how alkylphenol distributions in produced oils and waters can be used to constrain reservoir simulations and production processes (Bennett et al, 2007).

Generated initially by catalytic alkylation and isomerisation reactions in source rocks during petroleum generation (Ioppolo-Armanios, 1995; Taylor et al, 1997), they are effective migration tracers(Larter et al, 1996a), being removed by and constraining long range petroleum secondary migration (Larter and Aplin, 1995, Larter et al, 1996b; Lucach et al., 2002; Bennett et al, 2007). They are also removed by advanced levels of in reservoir biodegradation (Taylor et al, 1997 and figure 1). Fig 1 shows the C₀-C₃ alkylphenol distributions and summed concentrations in two putative oil sands contributor source oils, a long range migrated oil from the W. Canada heavy oil belt, a moderately biodegraded oil from the Peace River area and a severely biodegraded oil sand bitumen from the Athabasca oil sands. Note the absence of alkylphenols in the native reservoired Athabasca bitumen, while the non-biodegraded oils show appreciable quantities of alkylphenols. This non occurrence of phenols in native oil sands bitumens, may well account for the strongly water wet nature of the reservoir as alkylphenols have been shown to impact the occurrence of oil wet states in reservoirs (Bennett et al, 2007; van Duin and Larter, 2001).

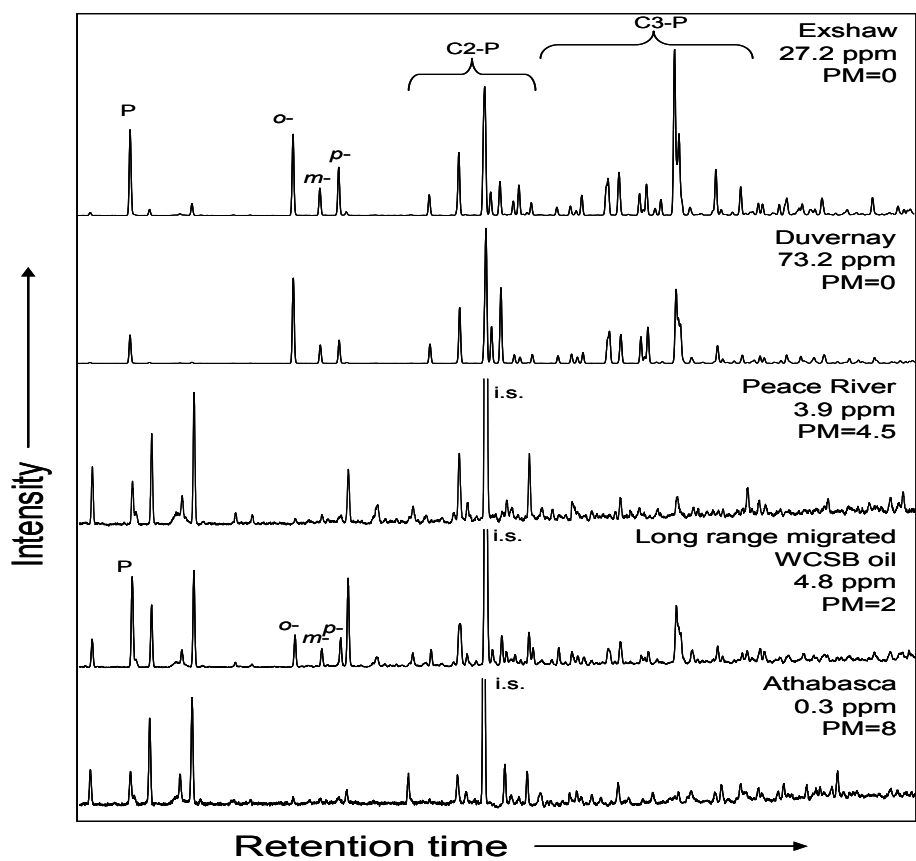


Figure 1: Partial reconstructed summed mass chromatograms (m/z 166, 180, 194 and 208) representing the C₀₋₃ alkylphenol distributions (analysed as TMS-ethers) and concentrations in 2 putative oil sands source oils (derived from Exshaw and Duvernay formations) and a moderately biodegraded Peace River oil, a severely biodegraded McMurray Fm oil sands bitumen and a long range migrated heavy oil. PM = level of biodegradation assessed using the Peters and Moldowan scale of biodegradation, PM0 = pristine oil, PM10 = very severely biodegraded; P = phenol, o- = ortho-cresol, p- = para-cresol, m- = meta-cresol.

While alkylphenols in crude oils are generated during catagenetic processes in the source rock, they can also be generated by anhydrous or hydrous pyrolysis of polar crude oil fractions containing phenolic or arylether species, including most crude oil asphaltenes (Larter and Douglas, 1980; Larter and Horsfield, 1993; Eglinton et al, 1991; Stalker et al, 1994) and are sometimes present in oils recovered from thermal recovery processes. The distributed activation energy kinetics of low molecular weight alkylphenol generation from coals under maturation processes are very well understood (Senftle et al, 1986; Larter, 1988, 1989) and if used as an analog for phenol generation from resins and asphaltenes and extrapolated to high temperature bitumen thermal recovery operation temperatures, this indicates alkylphenols would be expected as generated products of some high temperature thermal bitumen recovery processes. In general, while native bitumens contains C₀-C₃ alkylphenols at concentrations of typically less than 0.5ppm, thermally processed (e.g. pyrolysis) heavy oils and bitumens, or their polar fractions, can sometimes contain substantial concentrations of alkylphenols.

The four phase partition of alkylphenols in the system gas, oil, water, mineral has been studied (Taylor et al, 1997; Bennett et al, 1997; Bennett et al.,2003) and the high and carbon number variable vapor pressures of the C₀-C₃ alkylphenols, their high and carbon number variable water solubility and their carbon number variable solid phase partitioning characteristics, plus their neogenerated nature in some thermal recovery operations, means they are potentially uniquely able to constrain many aspects of recovery process system description including steam chamber saturations and fluid flow corridor geometries in an analogous manner as they have been used to monitor petroleum migration(Larter et al, 1996b). We discuss, using that theoretical model, how alkylphenols added to bitumen thermal recovery process fluid streams via injection, or generation during thermal recovery, might impact reservoir state or be used as quantitative tracers of reservoir state and multiphase flow behavior.

Conclusions

Phenols are small hydrophilic molecules that tell us much about the petroleum systems of Alberta and may have an important role in monitoring thermal recovery operations.

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