BIODEGRADATION RATES OF DIBENZOTHIOPHENES IN OILS: A CASE STUDY FROM THE LINPAN OIL FIELD, BOHAI BAR BASIN, EASTERN CHINA

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Introduction
This study focuses on the biodegradation rates of C0-C3 dibenzothiophenes (DBTs) in crude oils. Biodegradation of DBTs in oils are removed from level moderate (scale of Wenger et al., 2002) or level PM3 (scale of Peters, et al., 2005), and removed during scale of heavy and severe (PM5-10). However, our study of anaerobic experimental biodegradation has shown that the DBT and its homologues are removed synchronized with n-alkanes or even earlier (Shengbao Shi, et al., 2015, IMOG 2015).

The 6 oils with different levels of biodegradation were collected from the Linpan Oil Field, Bohai Bay Basin, Eastern China (Figure 1). Shallower reservoir horizons of theses oils suggesting the biodegradation likely occurred under the aerobic environment. The main source rock horizon of the oils is in the third member of the Shahejie Fm in the Eocene (Es3). The parameter Ts/Tm ranged from 0.45 to 0.73 shows that the maturation of all collected oils are similar, and the distances of the sampling wells are around 5 kilometres, suggesting the alterations of these oils attributed to biodegradation. Fractions separation and hydrocarbons GC-MS analysis follow the previous literature (Guangli Wang et al., 2016).

Results and discussion
Similar as alkanes in saturated hydrocarbons, most of aromatic compounds concentrations decreased to near the detection limit in collected oils, including naphthalenes, phenanthrenes, dibenzothiophenes, and dibenzofurans and their short alkyl-substituted compounds. Triaromatic steroid hydrocarbons are the most resistant compounds to biodegradation (Peters, et al., 2005). In present study, C26-triaromatic sterane was chosen as the non-biodegraded compound in oils. The degradation rates in this study are defined by relative concentrations of objective compounds to C26-TAS.

The results show that biodegradation of DBTs have started no later than biodegradation scale level PM2. The average 19.77% of DBT and C1-DBTs were degraded in the scale of PM2, and the value up to 38.43% in PM3, 77.01% in PM5, and more than 95.85% in PM6-10. C2-DBTs degradation rates are lower than C1-DBT, with average 19.21% degradation in PM2, 30.02% in PM3, 50.92% in PM5, and 67.51% in PM6-10. The biodegradation of more alkyl-substituted DBTs will be discussed in further study.

DBT is degraded as quickly as dibenzofuran (DBF) and phenanthrene, and the highest degradation rate of DBT is 97.34%, similar to 94.87% of DBF and 99.03% of phenanthrene in severely biodegraded sample P40-17. C1-DBTs highest degradation rates ranged from 91.41% to 98.07%. With lower degraded rate, the position 1 alkyl-substituted compound (far away from atom S) shows more resistant to biodegradation than other position substituted ones. C2-DBTs highest degradation rates ranged from 21.17% of 1,7-DMDBT to 97.88% of 3,6-DMDBT. Similarity to C1-DBTs, the C2-DBTs alkyl-substituted on 1, 8, and 9 positions have lower degraded rates than those on 4 and 6 positons, suggesting structural control of
molecular (Head, I.M., et al., 2003). The biodegradation sequence of C1-DBTs is 2+3- >4- >1-MDBT, and C2-DBTs have the sequence of 3,6-2,6->4,6-4-ethyl->1,4-+1,6->2,4->2,7+3,7->2,8->2,3+1,9->1,2->1,7.

Figure 1 TIC, m/z 191 and m/z 184+198+212+226+231 mass chromatograms of saturated and aromatic hydrocarbons in crude oils (a to f) with different biodegradation scale from the Linpan oil field (scale levels ranged from 0 to PM 6/or more severe).

References