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Conversion of inorganic chlorides into organochlorine compounds during crude oil distillation: myth or reality?

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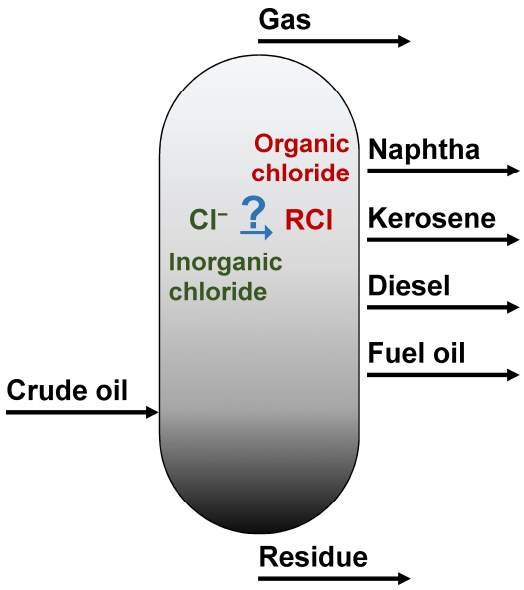
Abstract

In this short communication, we reinterpreted the experimental findings offered by Wu *et al.* about presence and distribution of organic chlorides in crude oil distillates (*Energy Fuels* 2015, 29, 1391−1396 and *Energy Fuels* 2018, 32, 6475−6481).

The results proposed by Wu et al. were examined employing a mass balance approach. From our preliminary analysis, we concluded that crude oil distillation may induce (significant) conversions of inorganic chloride into organic chlorides. Such an alteration in chlorine speciation could be relevant for managing corrosion issues in oil refineries.



In this note, we examine and partially reinterpret experimental findings offered in Wu *et al.*[1,2] about the presence of organic chlorides in crude oil distillates.

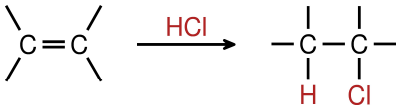
The assessment of amount, origin, distribution, and fate of chlorine compounds in crude oil is a key activity for understanding corrosion issues in refineries. When performing such an analysis, total chlorine in crude oil is usually speciated into inorganic chlorides ($NaCl + MgCl_2 + CaCl_2$) and organic chlorides (Σ RCl).

During fractional distillation inorganic chlorides can be hydrolyzed into HCl(g). This volatile gas (b.p. −85 °C) can migrate to the overhead condensers of the distillation tower, where it liberates corrosive H^+(aq) upon contact with water. The hydrolysis mechanisms of inorganic chlorides are well described in the literature.[3,4] It is reported that the kinetics of hydrolysis vary significantly among NaCl, $CaCl_2$, and $MgCl_2$: NaCl hardly liberates any HCl(g), whereas $CaCl_2$ and $MgCl_2$ are efficiently converted to HCl(g), being $MgCl_2$ the most susceptible to hydrolysis. $CaCl_2$ and $MgCl_2$ are also the most difficult to be removed by desalting. In a similar fashion, organic chlorides can also be converted into HCl(g) in presence of water at high temperature: $RCl + H_2O \rightarrow ROH + HCl$.[2,5] In crude oil, inorganic chlorides are usually associated with stable water-in-oil emulsions naturally present in the matrix, whereas organic chlorides are mostly related to anthropogenic contaminations.[6,7]

When evaluating corrosion issues induced by chlorine compounds, differences in terms of polarity, volatility, and hydrolysis rate between organic and inorganic chlorides must be carefully considered. Inorganic chlorides are water soluble salts, whereas organic chlorides are nonpolar compounds soluble in oil phase: only the inorganic fraction can be efficiently separated from oil matrix by means of traditional electrostatic desalters, whereas technologies for separating organic chlorides are still under development. Inorganic chlorides are non-volatile, therefore their corrosive action is mostly located in the distillation tower; on the contrary, organic chlorides are volatile, may accumulate in various distillation fractions and move along into other refinery units.

For example, organic chlorides in naphtha fractions are problematic for hydrotreating facilities where HCl can be liberated following hydrogenation: $RCl + H_2 \rightarrow HCl + RH$.[8,9]

Considering these differences in physical-chemical properties, accurate knowledge about the speciation of inorganic and organic chlorides in crude oil and its fractions is invaluable for the management of chlorine induced corrosion. For this reason, many analytical procedures,[10-19] including standard methods,[20-22] for chlorine speciation in crude oil can be found in the literature. A topic seldom addressed is the potential conversion between inorganic and organic chlorides within the refinery processes. In an interesting report from NACE, organic chlorides formation during crude oil processing was hypothesized from those materials containing high levels of contamination.[7] More recently, in an article by S. A. Treese about origin and fate of chlorides in hydroprocessing units,[9] addition reaction of HCl over olefins was regarded as a possible pathway for *in situ* generation of organic chlorides:



Scheme 1. Addition of HCl over the double bound C=C.

In fact, in most crude oils, olefins are present in the 0.3% to 10% range,[23] a great excess with respect to the HCl that may be generated from hydrolysis of inorganic chlorides. Although these conversions are chemically possible, extent and mechanisms of such reactivity within crude oil distillation are not well established.

In this context, we would like to comment on the data recently published by Wu *et al.* about the distribution of organic chlorides in crude oil after true boiling point (TBP) distillation.[1,2] We analyzed these data using a mass balance approach and we noticed that in one study[1] the TBP distillation induced the formation of organic chlorides following disappearance of the inorganic

ones. Our calculations are reported in the supporting information and summarized in Figure 1 and Tables 1-3.

The TBP process was carried out under conditions found in distillation towers where crude oil fractions were separated based on their boiling point. Wu *et al.* applied the TBP technique on two crude oils; both samples were initially characterized for total chlorine and inorganic chlorides by using industrial standards (method GB/T 18612-2001 for total chlorine and SY/T 0536-1994 for inorganic chloride); the organic chloride fraction was estimated by difference. After TBP distillations, all the fractions underwent a similar characterization.

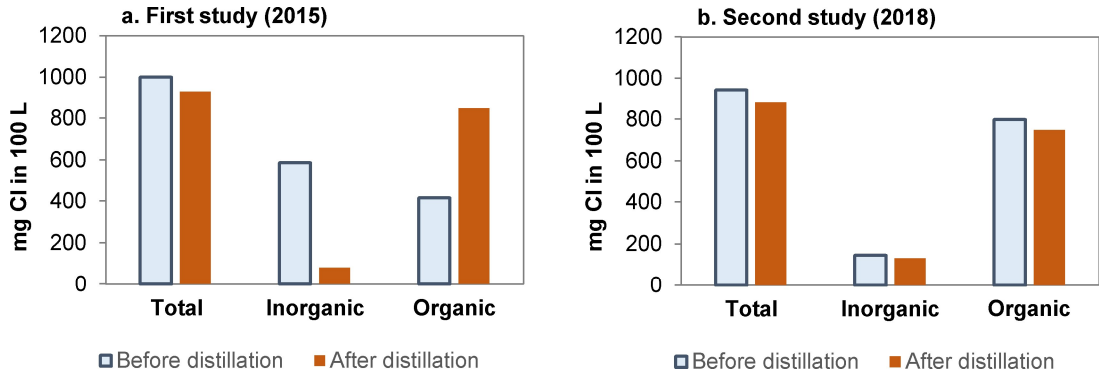


Figure 1. Mass balance of chlorine species in 100 L volume crude oil samples analyzed by Wu *et al.* in (a) 2015[1] and (b) 2018[2] *before* and *after* TBP distillation

Table 1. Mass balance of chlorine species in 100 L volume crude oil samples analyzed by Wu *et al.* in 2015[1] and 2018[2] *before* and *after* TBP distillation

Description	**Total chlorine** mg	**Inorganic chlorides** mg	**Organic chlorides** mg	**Inorganic/ organic** ratio
2015: Crude oil *before* distillation	1001.9	587.0	414.9	1.415
2015: *After* distillation, Σ(all fractions)	931.8	83.07	848.7	0.098
2015: Difference *after* - *before* (%)	−7.0%	−86%	+105%	
2018: Crude oil *before* distillation	944.9	146.0	798.9	0.183
2018: *After* distillation, Σ(all fractions)	881.3	132.7	748.6	0.177
2018: Difference *after* - *before* (%)	−6.7%	−9.1%	−6.3%	

Table 2. Calculating the mass of chlorine species in 100 L crude oil fractions using concentration values reported by Wu *et al.* in 2015[1]

b.p. range	**Yield**	**Total chlorine**	**Inorganic chlorides**	**Organic chlorides**	**Inorganic chlorides**	**Organic chlorides**	**Inorganic/ organic**
°C	vol (%)	mg/L	mg/L	mg/L	mg	mg	ratio
39.2 to 60	0.49	141.1	n.d.	141.1	n.d.	69.14	n.d.
60 to 80	0.58	58.62	n.d.	58.62	n.d.	34.00	n.d.
80 to 100	1.61	22.11	n.d.	22.11	n.d.	35.59	n.d.
100 to 120	2.25	9.180	n.d.	9.180	n.d.	20.66	n.d.
120 to 140	1.16	4.996	n.d.	4.996	n.d.	5.795	n.d.
140 to 160	1.81	3.517	n.d.	3.517	n.d.	6.366	n.d.
160 to 180	1.83	2.525	n.d.	2.525	n.d.	4.621	n.d.
180 to 200	2.09	2.446	n.d.	2.446	n.d.	5.112	n.d.
200 to 220	2.31	1.647	0.109	1.538	0.252	3.553	0.071
220 to 240	2.66	1.382	0.030	1.352	0.080	3.596	0.022
240 to 260	2.60	1.233	n.d.	1.233	n.d.	3.206	n.d.
260 to 280	3.41	1.782	n.d.	1.782	n.d.	6.077	n.d.
280 to 300	2.61	1.585	n.d.	1.585	n.d.	4.137	n.d.
300 to 325	4.45	2.234	0.043	2.192	0.191	9.754	0.020
325 to 350	4.31	1.965	0.076	1.889	0.328	8.142	0.040
350 to 375	4.61	1.781	0.080	1.701	0.369	7.842	0.047
375 to 400	5.01	2.112	n.d.	2.112	n.d.	10.58	n.d.
400 to 425	3.59	2.524	0.084	2.440	0.302	8.760	0.034
425 to 450	7.00	1.540	0.106	1.434	0.742	10.04	0.074
450 to 475	4.30	2.193	0.030	2.163	0.129	9.301	0.014
475 to 500	5.19	3.129	0.093	3.036	0.483	15.76	0.031
> 500	35.33	18.31	2.270	16.04	80.20	566.7	0.142
Sum	**99.20 L**				**83.07**	**848.7**	

n.d. = not detected (below detection limit)

As shown in Tables 1-3, on the basis of Wu *et al.* data, we could calculate the mass (mg) of total chlorine, inorganic chlorides, and organic chlorides found in 100 L crude oil before and after distillation. In the sample analyzed in 2018 (a desalted crude oil from Sinopec Beijing Yanshan

company), no large difference could be observed in chlorine speciation. Conversely, the sample analyzed in 2015 showed a marked change in the distribution of inorganic and organic chlorides: after TBP distillation a loss of 503.93 mg inorganic chlorides (−86%) corresponded to the formation of 433.8 mg organic chlorides (+105%). The total chlorine loss was only 70.1 mg (−7.0%), therefore the conversion of inorganic chlorides into organic chlorides, in this case, was the dominant chemical reaction involving chlorine.

Table 3. Calculating the mass of chlorine species in 100 L crude oil fractions using concentration values reported by Wu *et al.* in 2018[2]

b.p. range	**Yield**	**Total chlorine**	**Inorganic chlorides**	**Organic chlorides**	**Inorganic chlorides**	**Organic chlorides**	**Inorganic/ organic**
°C	vol (%)	mg/L	mg/L	mg/L	mg	mg	ratio
42.4 to 180	10.19	18.96	n.d.	18.96	n.d.	193.2	n.d.
180 to 230	5.87	7.633	0.130	7.503	0.763	44.04	0.017
230 to 300	10.15	6.592	0.120	6.472	1.218	65.69	0.019
300 to 350	9.05	3.158	0.150	3.008	1.358	27.22	0.050
350 to 500	27.76	2.365	0.180	2.185	4.997	60.66	0.082
> 500	35.64	14.03	3.490	10.04	124.4	357.8	0.348
Sum	**98.66 L**				**132.7**	**748.6**	

n.d. = not detected (below detection limit)

As reported in supporting information, we estimated the robust uncertainty of the concentration of organic chlorides. Since organic chlorides were evaluated by difference (total – inorganic) and the inorganic chloride was quantified with an apparatus able to provide results in the 0.2 to 10,000 mg/L range (NaCl), we assumed that inorganic chlorides concentrations reported in Table 2 were underestimated by a fixed amount of 1.2 mg/L Cl (tenfold above the detection limit of the instrument). Based on this assumption, we recalculated the data, and we still got similar results to those of Table 2. Considering the magnitude of the conversion, it is unlikely that such an effect could have been the result of an analytical artifact.

In the studies by Wu *et al.*, the GC-ECD characterization of organic chlorides in crude oil fractions was also presented. The main chlorinated species were industrial solvents such as carbon tetrachloride, trichloroethylene, and tetrachloroethylene. It is unlikely that fully chlorinated materials are originating from *in situ* reactions: with trace levels of inorganic chlorides in a 6 order of magnitude excess of hydrocarbons, one could expect that the conversion of inorganic chloride into organic chlorides would likely yield partially chlorinated derivatives. Considering the number of potential chlorinated compounds it would be a significant challenge to identify them by GC-ECD as the concentration of each chlorinated species would be very low when starting from mg/L levels of inorganic chlorides.

In conclusion, the computed mass balance data based on Wu *et al.* reports indicate the possibility of (quantitative) conversion of inorganic chlorides into organic chlorides during crude oil distillation.

Since these conclusions were underpinned only by a single published dataset,[1] further experimental work is required before drawing general interpretations about the conversion. In this regard, the role of matrix composition on the conversion will need careful assessment. For example, the data reported by Wu *et al.* referred to a light and a medium crude: only for the light crude conversion was relevant, whereas in the medium one the conversion was negligible (Figure 1). For further studies on the conversion of inorganic and organic chlorides in crude oil distillation, characterization of crude oil in terms of H/C ratio, bromine number, olefin content, and alkali composition seems to be important for a better understanding of the process.

ASSOCIATED CONTENT

Supporting Information

- Chlorine mass balance calculation (XLSX)

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