INTERNATIONAL JOURNAL OF
ENERGY AND ENVIRONMENT

Volume 1, Issue 6, 2010 pp.999-1008
Journal homepage: www.IJEE.IEEFoundation.org

Study of contaminants stemmed from the waste water of the Ivorian Refining Company

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Abstract
The dissolved hydrocarbons in waste water from the Ivorian Refining Company (SIR) are analyzed by means of a GC/MS coupling. The range of molar masses represented fairly fits the range of saturated hydrocarbons present in the treated crude oils. From this, it is deduced that solubility tables of pure hydrocarbons in water are not relevant for evaluating the risk of pollution propagation in the Ebrié lagoon. Aromatics are represented almost totally by toluene which is a molecule representing more than the half of total hydrocarbons. This particularity suggests that saturated hydrocarbons with high molecular weight found in the water form micelles with the toluene behaving as a surfactant. This molecule would be the main dispersion vector of hydrocarbons pollutants. The study of the ageing of these waters shows that they contain some agent responsible for biodegradation. These agents destroy the paraffins made soluble by the toluene.

Keywords: Hydrocarbons, Waste water, Biodegradation, Pollutants, Bacteria, Ivorian Refining Company (SIR), GC/MS, BTEX, KOW.

1. Introduction
Crude oil is a mixture of complex hydrocarbons and impurities such as sulphur-based compounds, oxygenated compounds, nitrogen-based compounds, inorganic salts and traces of metals. The oil refining processes contribute to water pollution. In addition to this, many chemical substances used in refineries, especially solvents, acids, caustic soda, corrosion inhibitors, detergents, etc. are also contaminants of effluents during draining or equipment washings. Nowadays, environmental issues are more and more taken into account in companies' activities and extensive research into ecology is carried out. In fact, oil exploitation has steadily increased since the beginning of the last century. Extraction, transportation and the use of this source of energy involve some risks of pollution of the marine environment and can sometimes degrade the ecosystem. Aquatic medium is a place where numerous substances directly or indirectly released by humans gather (substances released in the air or on the soil). Water pollution is a damage that makes it dangerous for use and harms the life in aquatic mediums, notably by successive contaminations of the food chain. Both surface waters and underground waters are concerned by the pollution. The purpose of this study is to analyze waste waters in order to identify and quantify different organic pollutants and find out their origins according to the industrial processes of the Ivorian Refining Company (SIR). The Ivorian Refining Company in Abidjan, Ivory Coast, is a refinery with a nominal distillation capacity of 3,500,000 tons per year, equivalent to 71,000 barrels per day. This refinery treats

crude oils mainly from Ivory Coast, Nigeria, Equatorial Guinea, Kuwait and Venezuela. The main production units of the Ivorian Refining Company are enumerated in the Table 1.

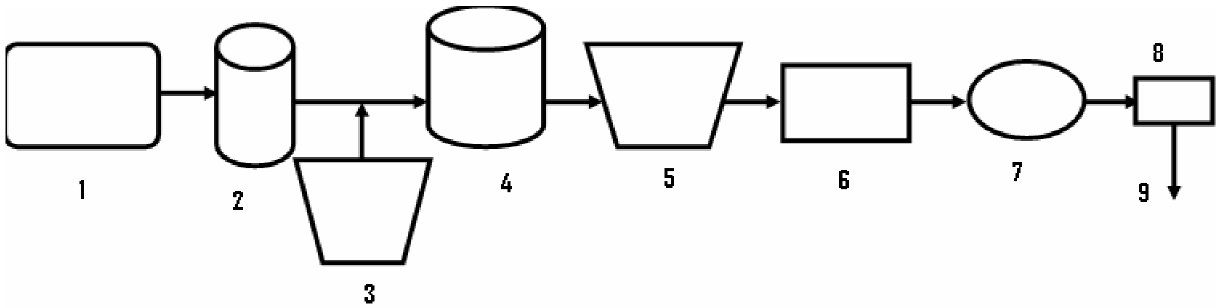
Table 1. The main production units of the Ivorian Refining Company (SIR)

Unit	Thousand of tons/year	Barrels per day
Atmospheric Distillation	3 500	71 000
Vacuum Distillation	1 650	33 000
Catalytic Reforming	450	9 000
HCU Distillation	650	13 000
Catalytic Hydrodesulphurization	550	11 000
Distillate Hydrotreating	700	14 000
Hydrogen Production		

The Ivorian Refining company is composed of five major complexes with the following units:

- The hydroskimming units (HSK2 and HSK3) where petroleum products such as gas oil, gasoline and kerosene are produced from crude oil;
- The hydrocracking complex DHC where gasoline, kerosene and gas oil are produced from the atmospheric residuum of the HSK2 and HSK3 units;
- The power station that supplies the refinery with electricity, water, steam, nitrogen, fuels and air. Waste water is also treated in this unit;
- The movements units that are in charge of products receiving and shipment. They also assure products transfer between the storage facilities and other units;
- The Multinational Bitumen Company (SMB) that produces bitumen and other petroleum products resold to the Ivorian Refining Company (SIR).

The hydroskimming units and the DHC are the main producers of waste water. Figure 1 describes the treating process flow of the waste water.



1. Salt remover, 2. Stripper, 3. Collecting tank, 4. T7 vat, 5. API tank, 6. flocculation drum, 7. flotator, 8. Observation tank, 9. release in the lagoon

Figure 1. Treating process flow diagram of waste water

The treating process comprises these 8 following stages:

1) Salts removing which consists of eliminating as much as possible mineral salts, water, mud, sediment and other impurities found in crude oil in order to reduce breakdowns, corrosion and fall in yield. Under the influence of a magnetic field, the electrodes inside the salt remover vibrate and provoke the coalescence of the water droplets dispersed as crude/water emulsion. The droplets get larger and fall to the tank bottom (water and impurities). This builds up oil droplets emulsion dispersed in a continuous aqueous mud (sand, clay …) Waste water coming from the salt remover is sent to the strippers for treatment. The salt remover is the major waste waters feed in the refinery.

2) The water stripping is a process during which steam is injected in order to extract the more volatile hydrocarbon pollutants. Stripped waters are then sent to a collecting tank.

In practice, only the hydrocarbons with a boiling point less than 100 °C are probably extracted. Therefore, it is only the gasoline fraction (C6-) that is extracted by means of this process. So, the stripper downstream flow contains dissolved salts, particles (sand, clay in suspension), low volatile oil droplets, and also possibly micro-emulsified hydrocarbons.

3) The collecting tank is the place where oily waters and other water wastes coming from polluted flagstones are collected. Then, they undergo a primary treatment (raking) for the removal of high-sized impurities.
4) The T7 vat is a pre-decantation place wherein come directly stripped waters. The mud at the bottom is extracted by means of a cleaning gate. A skimming device with three levels eliminates part of oils. Large mineral suspensions (sand) and drops of bitumen are eliminated as they are denser than water.
5) API tank:
At this stage, there are two API separators with a maximum flow of 2 × 150 m3/h where surface oils are trapped by two siphoned partitions. Floating drops less dense than water are eliminated after a decantation whereas at the previous stage, it was the denser substances that were removed. At this stage, the water contains micro-emulsified compounds, dissolved salts and all the fine particles which remain in suspension because of their surface potential (clay).
6) The flocculator
After the API stage, the water is pumped and sent to the flocculator where flocculants (cationic polymers and carboxymethyl cellulose) and coagulants salts of aluminium, iron, etc. are injected. The mixture is stirred by an agitator. The flocculated water flows to the flotator.
7) The flotator is the place where the water is mixed with pressurized air-saturated water, the expansion of which provokes the formation of micro air bubbles. The particles, that are likely to decant, accumulate at the bottom of the truncated part and are then evacuated towards the pit. The micro bubbles nucleate agglomerate of fine particle that are to be flocculated. As these particles are made up of clay (silicate denser than water), they sink and gather inside the truncated base where they are evacuated.
8) The observation tank
The treated water flows through the siphoned partitions of the flotator and, under the influence of gravity, goes down in the equilibrium column and then, in the observation tanks.

So, all of the waste waters treating process focuses on the removal of non-dissolved impurities, either solid impurities (sand, clay, sheets of bitumen, etc.) or liquid ones (oil droplets).
The pollutants that are completely dissolved (salts) and also the possible micro-emulsified clusters are not affected by stages 1 to 8. They are thus rejected through the pipes leading to the Ebrié lagoon. A high pollution of these waters could have harmful effects on the inside flora and fauna. The Ebrié lagoon is one of the fish reserves of Abidjan. That is why the public authorities are regularly analyzing these waters. The refinery strive for getting risks under control by meeting international standards and also by identifying causes and potential impacts in order to determine the best adapted technical solutions.
It is in this framework that the Ivorian Refining company gave us some samples of these waste waters. The samples were taken from the outlet of the treating tank in which polluted waters from different sources are collected.
This study focuses on the hydrocarbon pollutants stemmed from this refinery to the Ebrié lagoon. The gas phase chromatography technique coupled to a mass spectrometer (GC/MS) is used. This technique makes it possible to realize detailed assessment of organic species with some volatility (at least up to the C38 petroleum fraction).

2. Experimental protocol

2.1 The raw materials

The raw material is essentially composed of waste waters from the Ivorian Refining company. Some aliquots of the same samples have been analyzed at regular intervals of several months. At the receipt in Paris; say within a few days after sampling in Abidjan, the samples were contained by polyethylene flasks. They were then kept inside glass flasks in the dark at a temperature of 18 °C.

2.2 Description of the analysis equipment

The apparatus used is a GC/MS: Gaseous phase chromatograph STAR 3400 CX coupled to a mass spectrometer VARIAN-SATURN 4D: GC/MS/MS
It is composed of:
The column: A Restek apolar capillary column MXT100 (diameter 0.25 mm, 100 meters) is used. The pressure of the vector gas is equal to 200 kPa at the top of the column with a flow He of 0.8 ml/min. The initial temperature inside the column is 40 °C.

The oven: Temperature is programmed to vary from 40 °C to a maximum of 300 °C at a rate of 4 °C/min.
The injector: The injection from cold in the column is quickly followed by a rapid increase in temperature at a rate of 150 °C/min up to 250 °C, at which the system stays during 15 minutes.

2.3 The sample preparation
Hydrocarbon pollutants are first concentrated by about to a factor 200. This makes it possible to gain broader access to better accuracy in the analysis of dissolved molecular species in the waste waters. Hydrocarbons are quantitatively extracted by means of pentane. The extraction efficiency is improved by a salting out effect, mixing CaCl2 brine to each waste water sample. This salt improves the relative affinity of hydrocarbons for pentane. For 100 cc of waste water, 30 cc of $CaCl_2$ / H_2O 6M and then 5 cc of pentane are added. The mixture is agitated and set for pentane decantation. The pentane phase is then extracted. Another amount of pentane (5 cc) is added to the salty water. The mixture is agitated and set for decantation. The second pentane extract is added to the first one. An internal standard chlorobenzene at 1000 ppm in the pentane phase is then added. The total extract undergoes a slight evaporation at 35 °C until there remains to about only 0.5 cc solution. It is used as a standard in order to relate the analyses to water masses. Because of this evaporation, hydrocarbons, more volatile than heptanes are not quantitative.

3. Results and discussion
At the date of the sampling, the refinery was treating a heavy crude oil called Ebur. The composition of the Ebur has been determined by means of a GC/MS analysis and the results are shown on the Table 2.

Table 2. Composition of the Ebur crude oil in ppm

Carbons number	n-paraffins	Isoparaffins	Cyclo-alkanes	Conventional aromatics	Resins
6	5500	123	0	0	0
7	3989	7768	753	15	0
8	2996	2171	3026	667	0
9	2338	1344	2723	1427	0
10	2193	1230	3233	1098	0
11	1976	822	4720	1597	0
12	2085	624	6758	2964	0
13	2281	1525	9358	5706	0
14	2543	1815	11098	8828	0
15	2548	1999	12561	11594	0
16	2659	992	12255	13016	0
17	2286	2030	12336	12683	0
18	2208	2079	13137	11540	33
19	2188	1459	12558	10639	213
20	2720	566	11390	10716	917
21	3110	927	11058	11253	2594
22	3377	1093	10713	11597	4761
23	3415	1310	10529	11767	6567

Within the first approximation, the paraffin abundance is the same at any molar mass between 7 and 23 carbons.
Table 3 shows the composition and proportions of hydrocarbons according to family in the waste water sampled at the moment of the processing of this heavy crude oil.

Table 3. Composition of the waste water at the Receipt (0 Month) in ppm

Carbons number	Normal-paraffins	Isoparaffins	Cyclo-alkanes	Alkyl-benzenes
7	7	0	0	262
8	6	13	0	4
9	5	12	3	0
10	7	11	7	0
11	8	7	3	0
12	7	6	7	0
13	7	6	10	0
14	8	7	13	0
15	10	7	21	0
16	10	10	37	0
17	10	14	62	0
18	9	14	66	0
19	7	9	46	0
20	8	9	43	0
21	6	7	34	0
22	5	5	30	0
23	4	3	26	0
24	3	3	24	0
25	2	1	21	0
26	1	0	0	0

In this Table we can see that the molar mass range of hydrocarbons is very wide. Within the first approximation, the paraffin abundance also is the same at any molar mass between 7 and 23 carbons.
This would be unexpected in the case where thin distillation fractions such as semi finished products or finished products (gasoline, kerosene, gas oil, etc.) would have been contacted. Such direct water contact does not significantly contribute to the pollution.
The polluting paraffins molar mass bunch is very similar to the crude oil one. Despite of this, the polluting hydrocarbons perform a very different composition compared to the original crude one. In the polluting bunch, conventional aromatic alkanes are strongly depleted. Resins are nearly absent, and the conventional aromatics profile restricts to the light alkyl benzenes; say mainly toluene. Minor traces of mono and di-methyl substituted phenolic derivatives also are detected.
Finally, the water wastes are mainly polluted by toluene and saturates. This observation is very indicative of physical phenomena controlling the heavy hydrocarbon solubility.
All the heavy crude oils are aromatic and this is shown too on Table 2 in the case of the Ebur oil. Because aromatics are more polar than paraffins, intuitively one may forecast the presence of a larger quantity of heavy polar hydrocarbons in the waste waters pollutants. In fact, they are totally excluded. This means that a selective sorting out takes place.
The water solubility of the pure paraffins very strongly decrease when increasing the paraffin molar mass. As it is not the case in waste waters, this implies that those dissolved hydrocarbons are not at infinite dilution in the wasted waters but form micro clusters. Micro clusters of totally apolar compounds hardly would be more soluble than their constitutive elements. This implies the solubility of such clusters to be reached thanks to some surfactant.
Back to the comparison between Tables 2 and 3, the over-representation of toluene is flagrant, both in the composition of the extract and in comparison with other aromatics contained in the heavy crude oil. Its over-representation in the waste water suggests this molecule to be a good candidate as the surfactant that makes heavy paraffins soluble.
In the process of trying to explain why toluene is that much over-represented compared with other aromatics, two hypotheses can be formulated: Either there is somewhere in the refinery a place where water comes directly into contact with a virtually pure toluene, or micelles are formed directly from the crude oil in contact with water and their nanometric arrangement imposes that the hydrocarbon surfactant should be only slightly substituted aromatics.

There is no toluene production plant in the refinery. Furthermore, adding toluene to Ebur and performing the liquid-liquid equilibrium with pure water, it is observed the saturated hydrocarbon amount in the water phase to be strongly improved by the presence of toluene. As a consequence, most likely is the second hypothesis. Micro clusters of paraffins embedded with toluene basically are the way hydrocarbons solubilise when this kind of crude is put in contact with water.
Five months after receiving the samples and their first analysis, their possible time evolution is studied. The results of this second analysis are shown on the Table 4.

Table 4. Composition in ppm of the waste water after the second analysis (5 months)

Carbons number	Normal-paraffins	Iso-paraffins	Cyclo-alkanes	Alkyl-benzenes
7	0	0	0	247
8	0	0	0	4
9	2	0	0	0
10	2	6	2	0
11	3	5	2	0
12	3	6	7	0
13	1	7	9	0
14	1	6	16	0
15	3	9	40	0
16	6	13	58	0
17	7	16	93	0
18	6	16	91	0
19	5	10	72	0
20	5	5	46	0
21	4	5	39	0
22	3	4	31	0
23	2	3	21	0
24	1	2	24	0
25	1	1	23	0

The comparison is exhibited on Figure 2, focusing on n-paraffins.

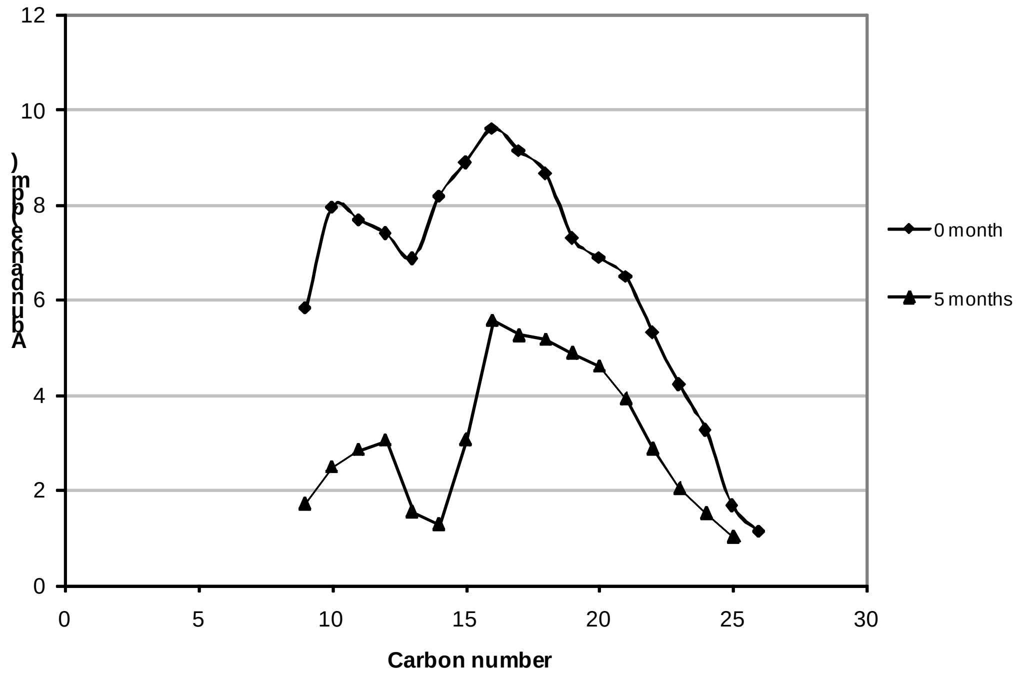


Figure 2. Abundance of n-paraffins in waste waters (in ppm)

The analysis of this graph shows a sharp decrease in the lightest (C_8-C_{10}) paraffins content of the waste water. The Figure also shows that the loss in hydrocarbons mass started since the first analysis (C_{11}-C_{13}) has substantially increased. The disappearance of n-paraffins being selective, it cannot be explained by the vaporization of light hydrocarbons. The depletion concerns paraffins that are usually liquid at ambient temperature with crystallization temperature regularly increasing with the molar mass. Thus, it is unlikely C_{12}-C_{13} n-paraffins to crystallize on the inner sides of the flask whereas simultaneously the C_{10}-C_{11} and the C_{14}-C_{15} do not.

The disappearance is selective within the range of molar masses. This phenomenon is well-known in subsurface petroleum reservoirs and generally attributed to biodegradation. So, the samples of waste water taken seem to contain some bacterial strains capable of degrading paraffins. The loss in hydrocarbon mass C_{11}-C_{13} noticed in November, that is to say a few days after the sampling in the refinery, suggests that the fermentation began very early, with biodegradation probably activated by the tropical climate of Abidjan.

Biodegradation of hydrocarbons has been underlined in 1946 [1]. Since that time, many bacterial species have been discovered and the most predominant are [2, 3]: Micrococcus, Corynebacteria, Pseudomonas, Acinetobacter, Alcaligenes, Vibro, Flavobacterium, Achromobacter, and Nocardia.

Among these bacteria, only the acinetobacter and the pseudomonas aeruginosa are specialized in degrading n-paraffins, whereas pseudomonas citronellolis is specialized in degrading ramified alkanes [4, 5].

Tables 5 and 6 below show other examples of bacteria capable of degrading some hydrocarbons.

Table 5. Examples of anaerobic bacteria degrading aromatics and aliphatic hydrocarbons

Bacterial species or strains	Metabolized hydrocarbons	References
Denitrifying bacteria		
Thauera aromatica T1	Toluene	[6]
Azoarcus tolulyticus Td 15	Toluene, m-xylene	[7]
Azoarcus sp. EB 1 strain	Ethylbenzenes	[8]
HxN 1 strain	Alkanes (C_{14}-C_{20})	[9]
Iron reducing Bacteria		
Geobacter metallireducens G15	Toluene	[10]
Sulfate reducing Bacteria		
Desulfobacula Toluolica	Toluene	[11]
Desulfobacterium cetonicum	Toluene	[12]
AK-01 strain	Alkanes (C_{13}-C_{18})	[13]

Scanning biodegradation on reservoir petroleum fluids, show that bacteria finally can metabolize all of the linear paraffins and mono-substituted hydrocarbons from hexane. But they have some food preferences. Generally, they firstly degrade the n-octane to n-dodecane region. But when scarcity comes along, they enlarge the bunch.

The gap observed here in the case of n-paraffins with a chain of 11 to 13 carbon atoms (C_{11}-C_{13}) and the sharp drop in the quantities of n-paraffins with a carbon chain containing 16 to 25 atoms may be related to the fact that n-alkanes with a carbon chain of 9 or more atoms are the hydrocarbons that are more easily degraded by a wide range of micro organisms [15].

3.1 Environmental consequences

The risk of spreading pollution is obviously higher for the more soluble molecules. For this reason, environmental norms focus on the solubility of pure pollutants in water. Secondarily, they focus on the risk of polluting fish fats, and the Kow parameter studied [16] is supposed to identify that risk. Just as solubilities [16], Kow only are defined on the share of a pure pollutant between water and octanol. Here, both these norms are irrelevant since solubilisation is mainly performed as micelles.

Pollutants to be spread in the lagoon are thus much more concentrated than expected. But this pollution only contains toluene as aromatics. This molecule is quite volatile. It is most probably transferred quite quickly to the atmosphere. The other hydrocarbons are saturated, say quite low toxicity hydrocarbons. Furthermore, most of them, paraffins, are destroyed by biodegradation within a few days.

Table 6. Micro-organisms capable of degrading petroleum hydrocarbons [14]

Contaminant	Micro-organism	Degradation potential
Benzene	Pseudomonas putida, P. aeruginosa, Acinetobacter sp., Methanogens, anaerobes	Moderate to high
Toluene	Methylosinus trichosporium OB3b, Bacillus sp., Burkholderia cepacia (ortho-monooxygenase), Pseudomonas putida, Cunninghamella elegans, P. Aeruginosa, P mildenberger, Pseudomonas sp.(also called thauera aromatica) Geobacter mettalireducens Desulfocula, Achromobacter sp., methanogens, anaerobes	High
Ethylbenzene	Pseudomonas putida, Pseudomonas sp. (also called thauera aromatica)	High
Xylenes	Pseudomonas putida. Pseudomonas sp (also called thauera aromatica) methanogens, anaerobes	High
Naphthalene	Pseudomonas putida	-
Alkanes	Pseudomonas oleovorans Methanosarcina barkeri	-
Kerosene	Torulopsis, Candidatropicalis, Corynebacterium hydrocarbociastus, Candidaparapsilosis, C. guillermondii, C. lipolytica, Trichosporon sp., Rhohosporidium toruloides, Cladosporium resinae	High

4. Conclusion

The waste waters of the Ivorian Refining Company (SIR) contain much higher concentrations of hydrocarbons than theoretically expected because they form micelles. Apart from toluene, those micelles mainly contains paraffins or paraffin substituted cyclo-(pentane/ hexane); say quite low toxicity hydrocarbons.

The waste water treatment at SIR do not allow for eliminating dissolved hydrocarbons provided non volatile. As a consequence these micelles are rejected in the Ebrié lagoon. In order to comply with environmental rules, especially in the Abidjan context where the lagoon is a fish reserve, efforts should be done in order to improve the waste water treatment in order to retain these micelles.

Acknowledgements

The authors thank the CNRS and the french-ivoirian office for cooperation of the MAE for financial support.

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