

# COMPOSITIONAL MODELLING OF GENERATION AND MIGRATION OF PETROLEUM COMPOUNDS IN A HIGH PRESSURE/ HIGH TEMPERATURE ZONE IN THE CENTRAL GRABEN (NORTH SEA): INFLUENCE OF THE THERMAL STABILITY OF CHEMICAL CLASSES ON THE OIL PREDICTION.

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## INTRODUCTION

Basin simulators that predict oil and gas generation and migration in petroleum systems use kinetic schemes of oil and gas production based on pyrolysis of source rock samples for simulating their natural maturation. The organic matter decomposition with increasing temperature due to burial in geological conditions is governed by kinetics, the thermodynamically stable ends being methane and almost pure carbon. As millions of reactions occur in source rocks, a number of product groupings and assumptions have to be done for modelling cracking kinetics, and several models have been described in the literature (1-7). The present study is a part of an European Union sponsored project associating BP, EEP and IFP. In this paper we simulate the generation, migration and cracking of fluids until present on the high pressure (1100 bars) high temperature (190°C) Elgin field in the North sea with the 2D simulator Temispack. We compared in the same 2D cross section a kinetic model 1 calibrated on pyrolysis and field data, describing kerogen cracking into two classes, oil and gas, and another kinetic model 2 calibrated on pyrolysis data only, based on various chemical classes with different thermal stabilities. Oil cracking is calibrated on pyrolysis data, giving gas and coke in model 1 and a chemical class distribution in model 2. The two models compute the genesis and secondary cracking of hydrocarbons in the source rocks, their expulsion, migration and secondary cracking in carriers and reservoirs, the saturations and number of phases in each element of the section. The present hydrocarbon composition observed in Elgin Fulmar sands reservoirs is compared with the corresponding results of these models and thus accounts for their difference in kinetic modelling.

## EXPERIMENTAL AND MODEL SETTINGS

### Geological context modelling

The studied zone is located in the 'four corners' high pressure high temperature area in the North Sea Central Graben. The choice of this zone was guided by the will to test the models in an unusual geological setting where present day conditions may seem a priori unfavorable to oil preservation, leading to question the kinetic schemes currently used in basin simulators. A 2D cross section intersecting the structural crest of the Elgin field as well as the relevant kitchen areas was reconstructed through time, the geological history of sediment deposition being described by a series of 31 events corresponding to stratigraphic markers. To each formation is associated during burial a lithology describing the compaction (porosity vs. depth), the conductivity and the permeability of the rock. The stratigraphic and lithologic parameters of the 2D cross section are given in Table 1. The parameters of lithologies and the thermal boundary conditions were calibrated on present day temperatures and pressures coming from well data, and on vitrinite reflectance measurements. The present day geometry and source rock position as reconstructed by Temispack is shown on Fig. 1.

### Geochemical parameters

#### a) source rock distribution

Pertinent information on the sedimentology of source rocks is crucial for a good prediction of oil and gas potentials. Previous geochemical studies in the Elgin area showed that main source rocks are within the Kimmeridge and Heather formations and contain marine organic matter (Type II of Tissot and Welte (8); organofacies B of Pepper and Corvi (6)). A second source rock can be found in the Pentland formation (Middle Jurassic). However its organofacies varies according to the studied zone from algal lacustrine (Type I/organofacies C) to coaly (Type III/organofacies F), making difficult to estimate at a regional scale the amount and petroleum potential of the formation. In the Elgin area, the Pentland source rock is considered as Type III organic matter bearing.

#### b) kerogen cracking parameters

As primary cracking of kerogen consists mainly in breaking of functional bonds, the kinetic parameters depend on the kerogen type. Both models describe kerogen and oil cracking by a set of parallel reactions, assuming that the order of all reactions is one and the rate constants follow the Arrhenius law. The distribution of partial potentials according to activation energies is Gaussian in model 1, thus defined by its mean and standard deviation and one preexponential factor; it is calibrated on pyrolysis experiments and field data. Oil (C<sub>6</sub>) and gas (C<sub>1</sub>-C<sub>2</sub>) generation are modelled separately. For model 2, a discrete distribution of partial potentials for increasing activation energies is calculated by an optimization procedure (9) to account for the Rock Eval

pyrolysis curve obtained with different heating rates; the preexponential factor is the same for all reactions and a reactive fraction of the total hydrogen index is calculated for each activation energy. In order to simulate hydrocarbon generation and migration, once geochemical types and amounts of possible source rocks are mapped, two options can be chosen. Either default cracking parameters are used on the basis of known geochemical data on the modelled area, or cracking parameters are adjusted on the pyrolysis study of representative samples. The first option is the only one possible for model 1. For using the second option, samples at the beginning of the catagenesis zone (oil generation) have to be recovered in sufficient amount. Their organic matter must be isolated from minerals to avoid undesirable catalytic effects due to the increase in temperature necessary for compensating geological time during the pyrolysis procedure. For calibration of the Kimmeridge and Heather source rock in model 2, an immature Kimmeridge clay from the Yorkshire coast was used for pyrolysis experiments. The immature equivalent of the Pentland Type III was not available, thus default kinetic parameters were used for this source rock. The complete methodology for determining the kinetic parameters of reference kerogens is defined in (10). The derived procedure used here for Type II kerogen in model 2 is summarized hereunder.

A first step is to perform compositional Rock Eval according to the method described by Espitalié et al. (11). Briefly, kinetic parameters are derived from pyrolyses at various heating rates in open system using an optimization procedure which determines for each kerogen an unique frequency factor and a weight distribution, for a discrete series of activation energies, of  $C_1$ ,  $C_2$ - $C_5$ ,  $C_6$ - $C_{14}$  and  $C_{15+}$  classes, using various cold traps. This step allows to compare the primary cracking of the type II kerogen into gas ( $C_1$ - $C_4$ ) and oil ( $C_{6+}$ ) between models 1 and 2. Model 1 is centered on  $E = 51$  Kcal/mol with a preexponential factor  $A = 8.14 \cdot 10^{13}$  s<sup>-1</sup> for oil and on  $E = 67$  Kcal/mol with a preexponential factor  $A = 2.17 \cdot 10^{18}$  s<sup>-1</sup> for gas. Model 2 is strongly asymmetrical and maximizes on  $E = 52$ - $54$  Kcal/mol for oil and on  $E = 54$  Kcal/mol for gas with a same preexponential factor  $A = 1.6 \cdot 10^{14}$  s<sup>-1</sup> for oil and gas. Although these models give very close generation curves in the laboratory conditions, it can be seen on Fig. 2 that it is no longer true in basin conditions, where the proportion of gas and oil are calculated for a constant sediment burial of 50 m/My and a geothermal gradient of 25 °C/km.

The second step consists in running preparative pyrolysis as described in (10), in order to quantify by gas chromatography the  $C_6$ - $C_{14}$  fraction into saturates and aromatics, and by weighing the  $C_{15+}$  compounds after fractionation by liquid chromatography into  $C_{15+}$  saturates,  $C_{15+}$  aromatics and NSO compounds. These proportions are applied evenly to the  $C_6$ - $C_{14}$  and  $C_{15+}$  classes obtained in the first step whatever the activation energy, as it was shown (10) that the pyrolysate composition does not change during open system pyrolysis.

A third step is to run gas chromatography on the  $C_{15+}$  saturates and to measure in the same carbon interval the total area of the chromatogram once the blank is subtracted, and the total area of *n*-alkanes and 1*n*-alkenes. The ratio of these areas gives the proportions of *n*-alkanes and *iso*-*cyclo*-alkanes in the  $C_{15+}$  saturates. Separation of these compounds in the kinetic scheme results from a recent study (12) on the effect of pressure on cracking of pure *n*- $C_{25}$ , showing that pressure in the range 100-800 bars has little influence on cracking kinetics compared to temperature. The influence of pressure was assumed to be small for all chemical classes. Absolute kinetic parameters were obtained, showing that *n*-alkanes are more stable than *iso*-*cyclo*-alkanes. These kinetic parameters are used for all  $C_{15+}$  *n*-alkanes. Because using pure compounds does not automatically take into account the mixture effect (hydrogen donors/acceptors), another study was performed to test this parameter (13), indicating that this effect does not change significantly the kinetic parameters and tends to delay cracking.

The final step is to perform an isothermal pyrolysis in closed system at 550°C during 24 hours on a kerogen at the beginning of the metagenesis stage. It was in fact shown (10) that open and closed system pyrolyses give fairly similar results for stoichiometric coefficients of primary cracking except for methane. In the open system the final pyrolysis temperature is higher than in the closed system and results in a competition between C-C and C-H bond cracking in the kerogen. The molecular hydrogen that is generated lowers the amount of methane. The kerogen at the beginning of the metagenesis stage may be either prepared on a natural sample, or preferably by performing a first pyrolysis on the immature sample at 350°C during 48 hours to generate all the oil from primary cracking, then extracting the remaining kerogen. The  $C_1$  and  $C_2$  gases being stable in geological conditions can be quantified after the second pyrolysis, allowing to split the gas into  $C_1$ ,  $C_2$  and  $C_3$ - $C_5$ .

This methodology results in a complete compositional description of the products of kerogen cracking into chemical classes of compounds. Even if these chemical classes represent the lumping of a great number of compounds, they behave similarly during secondary cracking because of similar chemical structures and bonds. The kinetic scheme for secondary cracking can thus be better constrained. In basins where source rocks do not experience a strong secondary cracking, this kinetic model can be highly simplified.

#### c) oil cracking parameters

Secondary cracking of oil consists mainly in breaking of C-C bonds, hence it does not depend on the kerogen type. In our work, we used standard secondary cracking schemes that were calibrated on pyrolysis experiments on isolated oils and mixtures of kerogen and its cracking products.

Model 1 uses as for kerogen a Gaussian distribution of activation energies, thus secondary cracking is defined by three parameters, the mean energy  $E = 58$  Kcal/mol and its standard deviation and a preexponential factor  $A = 10^{14}$  s<sup>-1</sup> (7). Oil cracks into gas and coke. Model 2,

presented in detail in (5), describes cracking of each chemical class defined previously by a reaction producing other chemical classes. The kinetic parameters, E, A and the stoichiometric coefficients are fitted on experimental pyrolysis values, and constrained by mass and atomic balances; the model is simplified by choosing the same preexponential factor for all reactions. This kinetic scheme (5) was modified in the present study by adding the cracking reaction of *n*-alkanes with its own E and A (12).

## RESULTS AND DISCUSSION

Once the 2D cross section was calibrated to match the pressure and temperature data, several compositional runs tested the influence of geochemical parameters on the saturation and composition of fluids in possible reservoirs. Typically, runs with model 1 need 10 hours and runs with model 2 need 25 hours of CPU on a Sun Spark Ultra 1 workstation. This difference is linked to the number of unknowns that have to be computed.

### Geological events

As shown on Fig. 1, during the Quaternary (1.64 My), over 1000 meters of silty shales were deposited. This large input of sediments resulted in a very rapid burial of the petroleum system. Fig. 3 shows the thermal history of the Fulmar sands, the reservoir of the Elgin field located just under the Kimmeridge and Heather source rocks. In this reservoir, the temperature increased from 160 to more than 180°C in the last million years. Due to the very low permeability of the carbonates in the Hod formation, the fluid expulsion was not quick enough to accommodate the rapid burial, enabling fluid pressures close to lithostatic pressure in the underlying sediments.

### Saturations and phase behaviour

The petroleum system modelling through time indicates that the Elgin reservoir filling begins around - 50 My. The petroleum fluid is monophasic during migration, thus all hydrocarbons, either C<sub>6+</sub> or C<sub>1</sub>-C<sub>5</sub>, move with the same speed.

### Primary cracking

The separate contribution of each source rock to the reservoir filling was tested. The results show that primary cracking is completed whatever the source rock considered, hence the oil composition does not depend much on the kerogen type. However as *n*-alkanes are fairly stable, their characteristic carbon distribution according to the source rock contribution, particularly in the Type I Pentland in other zones of the study, can still be recognized in the oil analyses.

### Secondary cracking

Its kinetic parameters determine the hydrocarbon composition in the Elgin reservoir. Model 1 predicts only gas; model 2 predicts both oil and gas. The oil composition predicted by model 2 and observed in the Elgin oil is shown on Fig 4. The prediction is fairly good for all chemical classes except for methane which is underestimated, and condensed aromatics which are overestimated.

The reason why model 1 overestimates secondary cracking can be found in the way it is mathematically expressed and calibrated. The Gaussian distribution of activation energies may be a reason as in many oils, saturates are both the most abundant and the most stable compounds. The calibration of cracking experiments is done by pyrolysis-gas chromatography. This technique allows the analysis of small amounts of hydrocarbon compounds to be performed but no mass balance can be made: only compounds able to cross the chromatographic column are detected. Heavy fractions are thus not taken into account, and this may bias the description of cracking, thus the mean activation energy, towards the light ends.

The methane underestimation of model 2 could be due in part to its quantification in primary cracking. Although the Rock Eval value has been corrected using the result of a closed system pyrolysis at 550°C/24h, a currently performed research shows that this correction represents only 60% of the total methane potential of the kerogen. Condensed aromatics are probably the least constrained chemical class in the secondary cracking scheme (6). Their definition was based on elemental analysis but the low amounts obtained during pyrolyses made it difficult to calibrate correctly the stoichiometric coefficients, and the activation energy may be too high, as already noticed in (6): 59.1 Kcal/mol for type II and III kerogens as compared with 57.1 for Boscan oil.

### Evolution of the petroleum system

The petroleum system modelling shows that the occurrence of oil in Elgin despite the presently high temperature is due to its very recent increase from 160 to 190°C in the last million years. This situation evolves rapidly as shown both by the model and by optical studies on reservoir cores proving that pyrobitumen due to the oil cracking is currently forming.

## CONCLUSION

Simulating generation, migration and entrapment of hydrocarbons in a petroleum system is the only way to handle its numerous variables and to be able to test the influence of selected parameters. Many of them depend upon assumptions which are sometimes uncertain; however the simulation allows us to check the current hypotheses, to measure the sensitivity to parameter changes and to calibrate the entry parameters against field data.

In this respect the present study shows that in a petroleum system where high temperature causes a large amount of secondary cracking both in source rocks and in reservoirs, it seems difficult to predict the occurrence of oil or gas without taking into account the detailed chemical composition of products, linked to their thermal stability, as done in model 2. It shows also that in this latter, the calibration of secondary cracking should be improved to better account for a higher proportion of

methane and a lower proportion of condensed aromatics. Future work will be performed in two directions: one is to run new pyrolyses on the oil constituents generating condensed aromatics, such as NSO compounds; it seems also necessary to check again the database and the optimisation procedure used to establish the secondary cracking scheme. The second consists in adjusting modified cracking parameters to the present study and then checking whether they are able to account for observed compositions in reservoirs from various sedimentary basins.

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n°	stratigr. markers	Age (My) (Top)	Stratigraphy	Lithology
1	Seabed	0	Quaternary	Shale_silty
2	T_Plio	1.64	Pliocene	Shale_silty
3	TE_Plio	3.4	Pliocene	Shale_silty
4	T_Miocene	5.2	Miocene	Shale_silty
5	T_Mid_Mio	10.4	Miocene	Shale_silty
6	T_Oligoc	23.3	Oligocene	Shale_silty
7	TMid_Eocene	38.6	Eocene	Shale_silty
8	TEar_Eocene	50	Eocene	Shale_silty
9	T_Balder	54.5	Palaeocene	Shale
10	T_Forties sd	57	Palaeocene	Sand
11	T_Maureen	61	Palaeocene	Shale_silty
12	T_Ekofisk	63	Maastricht.	Chalk
13	T_Chalk	65	Campanian	Chalk
14	Intra Chalk	71	Campanian	Chalk
15	T_Hod	78	Turon/Campan.	Arg_Lmst.
16	Intra Hod	81	Turon/Campan.	Hardgrds
17	int_Hod	83	Turon/Campan.	Arg_Lmst.
18	T_Herring	85	Cenom/Turon.	Plns_Marl
19	T_PlensMrl	90.4	Cenom/Turon.	Plns_Marl
20	T_Rodby	97	Albian	Tight_shale
21	T_Sola	112	Apitian	Shale
22	Kim_Clay	145.6	Portland/Berria.	KCF
23	Heather_shly	152	Oxford/Kimmeri.	Heather_src
24	int_Heather	153.5	Oxfordian	Shale_silty
25	Fulmar sdy	155	Callov/Oxford	Sand
26	Pentlnd-sdy	157	Bathon./Callov.	Shale&Sand
27	Pentlnd-shly	182	Bathon./Callov.	Pentland_src
28	Tr_Skagerrak	208	U.Triassic	Shale&Sand
29	Tr_Smithbank	222	L.Triassic	Shale_silty
30	Top_Salt	245	Zechstein	Salt
31	Rotliegend	256	M-L.Perm.	

Table 1: Stratigraphic and lithologic parameters of the 2D section

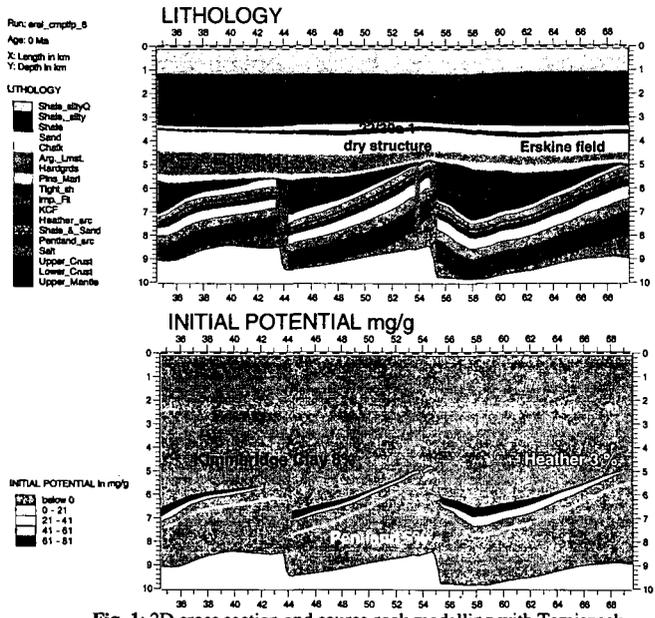


Fig. 1: 2D cross section and source rock modelling with Temispack.

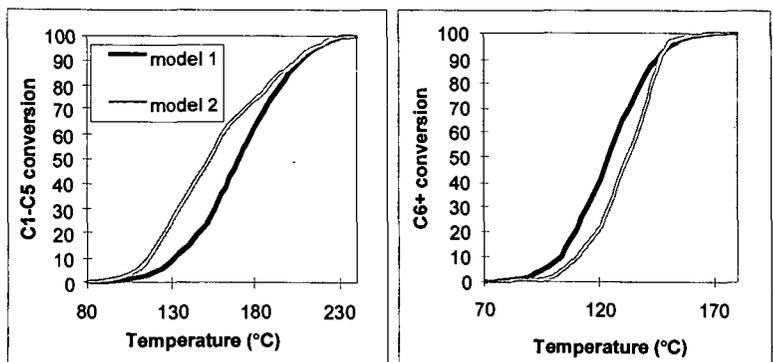


Fig. 2: Comparison of primary cracking kinetics in model 1 and model 2 calculated for a constant sediment burial of 50 m/My and a geothermal gradient of 25 °C/km.

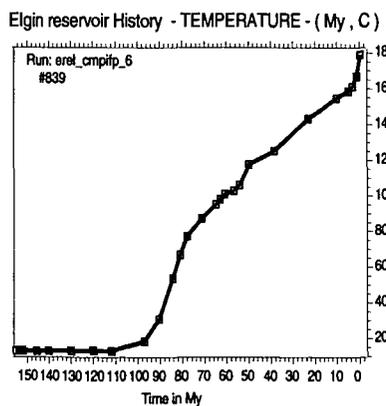


Fig. 3: Thermal history of the Elgin reservoir.

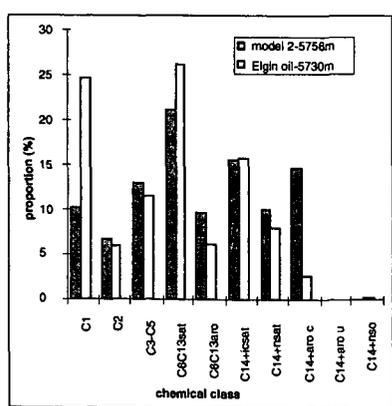


Fig. 4: Comparison of calculated and observed oil composition.