Up to what temperature is petroleum stable?
New insights from a 5200 free radical reactions model

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Abstract

The discovery of crude oils and condensates at ever higher temperatures casts doubt on the validity of the usual geochemical modelling approach, that uses empirical reactions and rate constants. The solution used to account for such a high thermal stability is presently to adjust the rate parameters, but the physical meaning and scientific value of such a strategy can be questioned. We have developed a mechanistic model consisting of 5200 lumped free radical reactions to describe the thermal evolution of a mixture of 52 organic species meant to represent light petroleum. Rate constants used are those available in the literature or estimated using well established thermochemistry-reactivity correlations. Chemical structures included in the model are linear, branched and cyclic hydrocarbons, hydro- and alkyl-aromatics, PAHs, and three heteroatomic compounds. Reactions include cracking and alkylation chains and inhibiting and accelerating reactions from the various reactants. This model has been applied to several mixtures with various proportions of reaction inhibitors and accelerators, and to a composition representing a light mature oil. From the results obtained, we conclude that mature oils will be stable up to 240–260 °C, depending on their composition, and that the thermal cracking of oil to gas is not possible under reasonable basin conditions. The kinetics of petroleum cracking are thus much slower than generally recognized.
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1. Introduction

For several decades, numerous efforts have been devoted to the kinetics of the thermal evolution of organic compounds in the Earth's crust. From a purely scientific point of view, this is necessary to understand the geological carbon cycle. From an economical as well as scientific standpoint, this is necessary to predict the commercial value of a suspected oil field. A critical question of particular concern for hot prospects (>170 °C) is whether oil or gas would be found, and

until the early 1990s, most studies concluded that only gas could be found under those conditions.

Such conclusions were mostly based on the kinetic modeling approach proposed by Tissot (1969), and further developed by Tissot and Espitalié (1975). That approach was initially intended to describe and predict oil generation from source rocks and variations of the method have been used extensively by numerous authors (e.g. Waples, 1984; Cooles et al., 1986; Burnham et al., 1987; Ungerer et al. 1988; Braun and Burnham, 1992). The core idea is to regroup organic constituents in families and to describe petroleum formation by global reactions whose stoichiometric coefficients and rate constants were determined empirically from laboratory experiments, usually performed in the temperature range $T = 350–500$ °C.

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The method has also been adapted to model the secondary cracking of petroleum in reservoirs (e.g. Béhar et al., 1992; Kuo and Michael, 1994; Pepper and Dodd, 1995), where petroleum compounds were divided into families that often resembled, for example, those used by Kuo and Michael (1994): C1 (for CH_4); C2 (for C_2H_6), C3–C5, (for hydrocarbons having 3 to 5 carbon atoms); C6-C14; stable aromatics (for benzene, toluene, xylenes and naphthalene), $C_{15}+$ saturates, $C_{15}+$ aromatics, resins, asphaltenes, and coke. Global reactions that described exchanges between these families usually considered that species such as CH_4, coke, and benzene were completely stable. These models usually predicted that extensive oil transformations were taking place at 160 °C. The model of Kuo and Michael (1994) applied to a waxy oil (Pematang) thus predicted that, with a heating rate of 1 °C per million years (Ma), all resins and asphaltenes would have disappeared at 160 °C, while concentrations of $C_{15}+$ saturates and of $C_{15}+$ aromatics would be reduced by about half and two thirds, respectively. At 200 °C, only wet gas (up to C_5) and coke were remaining. Surprisingly, the model predicted that no CH_4 would be formed at 200 °C.

Since the mid 1990s, the view that extensive cracking was taking place at 160 °C, and that almost complete transformation to wet gas and coke was achieved at 200 °C has been challenged by the discovery of light oils that were preserved at $T > 190$ °C in the North Sea (Pepper and Dodd, 1995; Vandenbroucke et al., 1999) and by the observations that oils reservoired at 175 to 200 °C showed little or no sign of thermal degradation (McNeil and BeMent, 1996). To resolve the unsatisfactory predictions of an oil cracking model, a possibility is to adjust the rate constants so that the model will yield adequate results. Since those rate constants are empirical and have no physical meaning (Dominé and Enguehard, 1992; Dominé et al., 1998), adjusting them is indeed within what is permitted by those models.

Recently, Vandenbroucke et al. (1999) have modeled the stability of the petroleum found in the Elgin oil field (North Sea), whose reservoir is at about 190 °C, using the approach just described. The authors claimed that their model successfully reproduced the stability of the Elgin fluid around 190 °C, and that this success could be viewed as an improvement in the method, that validate it even for hot prospects. However, their model used a combination of rate constants determined by a variety of methods. For example the rate constants for most of their reactions were determined by fitting the results of closed system pyrolyses of oils other than the Elgin fluid (this fluid will now be referred to as ELGIN), but the rate constant for the destruction of normal alkanes was taken from the results of pyrolyses of pure n–$C_{25}H_{52}$. Such a procedure is questionable. It is indeed well known that the apparent pyrolysis rate constant of a hydrocarbon depends on the composition of the mixture where it is diluted. For example, Khorasheh and Gray (1993) have shown that the pyrolysis of n–$C_{16}H_{34}$ was greatly hindered by the addition of tetralin, a constituent of petroleum, and Yoon et al. (1996) have shown that various additives could reduce the pyrolysis rate of complex hydrocarbon mixtures by factors that depended on the additive. In the case of natural organic mixtures, Burnham et al. (1997) and McKinney et al. (1998) also demonstrated by laboratory pyrolyses that the rate of pyrolysis of n-alkanes was affected by the composition of the oil matrix. It is thus erroneous to assume that a rate constant measured in a chemical environment can be applied to another one.

In any case, since rate constants used in the approach discussed here can be adjusted, it is obvious that one can always find a set of rate constants that will give the desired result. While it can reasonably be claimed that the approach developed by Tissot (1969) and Tissot and Espitalié (1975) has a good a posteriori descriptive value, it appears difficult to argue that it has a predictive value.

The purpose of this work is to propose a new modeling approach that will have a predictive value. It is based on elementary free-radical reactions, that can describe adequately the transformations of most species found in mature oils (Ford, 1986; Weres et al., 1988; Dominé, 1989 and 1991; Jackson et al., 1995; Bounaceur et al., 2000). In fact, Dominé et al. (1990) were the first to use a free-radical reaction mechanism under geochemical conditions to test the stability of hydrocarbons in reservoirs. Their model of hexane pyrolysis already showed that pure hydrocarbons were much more thermally stable than expected: they predicted that hundreds of million years would be required to reach a detectable thermal destruction of hexane at 160 °C. This result was achieved by using reaction rate constants measured in the laboratory for each reaction type used, and the parameters were therefore not adjustable, which contributes greatly to a predictive value of their approach.

It thus appears of great interest to explore the possibility of modeling complex hydrocarbon mixtures with a large number of free-radical reactions. Validation of such a model can be done by performing laboratory experiments at temperatures that allow observable changes on laboratory time scales, but considering our objectives, this will be a necessary but not a sufficient validation. This and future work should also compare the predictions of such a model with present observations on reservoirs around 200 °C. If predictions and observations agree after laboratory validation, then it can be envisaged that this complex free radical reaction model can be used as an efficient predictive tool in petroleum exploration.

2. Model

2.1. General concept

Thousands of species, most of which have not been precisely identified, make up petroleum. Each one of these species undergoes hundreds or thousands of free radical reactions. For example, modeling hexane pyrolysis at low conversion only (Dominé et al., 1990) required 156 reactions. Billions of reactions then take place in the thermal transformations of petroleum, and building a model will require drastic simplifications. These will be made by limiting the number of constituents of the model mixture chosen, and by lumping reactions. The reaction mechanism will first be written using an automated procedure for each individual selected species, and the number of reactions will be reduced by lumping. The mechanism of reactions of simple mixtures will be combined by adding the individual mechanisms and the relevant cross reactions. Species will then be added incrementally to the mixture, adding their own reactions and cross reactions with other species to the mechanism. The resulting mechanism will then be used to model several simple mixtures, and finally a crude oil, whose thermal stability will be determined.

2.2. Model mixture chosen

Because our purpose is to determine the thermal stability of oils, we will focus on mature oils, whose asphaltenes and resins contents are low. These macromolecules are not always well characterized, even though new data has recently been obtained on their structure (Strausz et al., 1999a, b), and modeling their thermal behavior in detail is difficult. We will then model an oil composition by attempting to mimic the composition of a mature oil such as ELGIN (Vandenbroucke et al., 1999). We have also obtained a sample directly from the Elgin well-head and analyzed it in detail, in order to identify all C_8- compounds, most C_{12}- compounds, and numerous others.

Based on these data, we propose to mimic the composition of a mature oil by the 52 species shown in Table 1. Species selected are linear alkanes C_1–C_{30}, that are ubiquitous in oils. Longer chain alkanes are only present in small or undetectable proportions in mature oils, and their behavior is similar to that of lighter ones. Branched alkanes are represented by 10 species: 8 are in the C_4–C_{12} range with one or two branched methyl groups, and pristane and phytane have been added to this family. Naphthenes are represented by propylcyclopentane and propylcyclohexane, and hydroaromatics by 1-methyl-indane and tetralin. Aromatics are represented by benzene, toluene, and naphthalene, that are often considered stable (Kuo and Michael, 1994) and by

butyl- and decyl-benzene, that are less stable (Savage and Klein, 1987; Dominé, 1991). These 49 species represent most identified hydrocarbon structures found in mature oils.

The problem is to represent resins and asphaltenes, whose structures are not known. Resins contain heteroatomic structures, that may contain chemical bonds weaker than those of hydrocarbons, and that may act as reaction accelerators and enhance oil degradation (Dominé et al., 1990). It is then essential to include such structures here, and we have selected three species with different bond strengths and potential accelerating effects: hydrogen sulfide, isopropyl-mercaptan, and diisopropyl-disulfide. These compounds are not very thermally stable and have not been detected in mature oils, so their inclusion can be questioned. In mature oils, sulfur is mostly trapped in very stable structures, such as dibenzothiophenes (Hughes, 1984), that will not act as accelerators and may not even have much impact on chemical reactions, so that their inclusion here is not crucial. However, we wish to include accelerators to evaluate their potential effects. These sulfur compounds can then be viewed as representative of possible reaction accelerators in oils. If we conclude that accelerators have little impact in mature oils, then we will have the option to set their concentrations to zero in model runs.
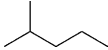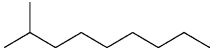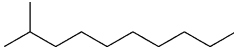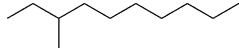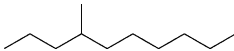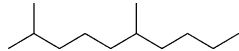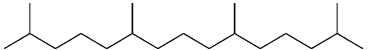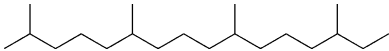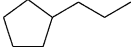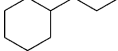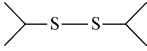
Asphaltenes are often viewed as consisting mostly of polyaromatic rings and alkyl chains (Savage and Klein, 1987; Strausz et al., 1999a, b). We represent them here, albeit imperfectly, by naphthalene and decylbenzene. Alkyl-naphthalenes will also be produced by our mechanism, which slightly increases the resemblance with asphaltenes. The hydroaromatic and naphthene stuctures present in asphaltenes (Savage and Klein, 1988) are also represented here.

It is clear that the 52-species mixture of Table 1 is not a perfect representation of mature oils, and no limited mixture can be. It does, however, contain most structures identified in such oils. Further work will benefit from faster computers, and adding extra species will be possible.

2.3. Generation and reduction of the reaction mechanism

Most of the 52 species used in this model are alkanes and we will illustrate the construction of the model with the example of alkanes. Modeling alkane pyrolysis at geochemical temperatures has already been detailed by Dominé et al. (1990, 1998) so only the main aspects will be recalled here. As shown by reactions (1) to (7), regrouped in Fig. 1, the reaction scheme of an alkane µH is made up of chain reactions leading to two cracking products, an alkane lighter than µH, βH, and an alkene, and to an alkylation product which is an alkane heavier than µH, here called alkane+. Recombination reactions also form products, but in negligible quantities, so that the

Table 1
Species included in the mixture that mimics a mature oil

Name	Formula	Structure
Alkanes		
30 linear alkanes	CH_4 to $C_{30}H_{62}$	
Isobutane	C_4H_{10}	
Isopentane	C_5H_{12}	
2-methylpentane	C_6H_{14}	
2-methylnonane	$C_{10}H_{22}$	
2-methyldecane	$C_{11}H_{24}$	
3-methyldecane	$C_{11}H_{24}$	
4-methyldecane	$C_{11}H_{24}$	
2,6-dimethyldecane	$C_{12}H_{26}$	
Pristane	$C_{19}H_{40}$	
Phytane	$C_{20}H_{42}$	
Naphthenes		
Propylcyclopentane	C_8H_{16}	
Propylcyclohexane	C_9H_{18}	
Hydroaromatics		
Tetralin	$C_{10}H_{12}$	
1-methylindane	$C_{10}H_{12}$	
Aromatics		
Benzene	C_6H_6	
Toluene	C_6H_8	
Butylbenzene	$C_{10}H_{14}$	
Decylbenzene	$C_{16}H_{26}$	
Heteroatomic species		
Hydrogen sulfide	H_2S	
Isopropyl mercaptan	C_3H_8S	
di-isopropyl disulfide	$C_6H_{14}S_2$	
PAH		
Naphthalene	$C_{10}H_8$	

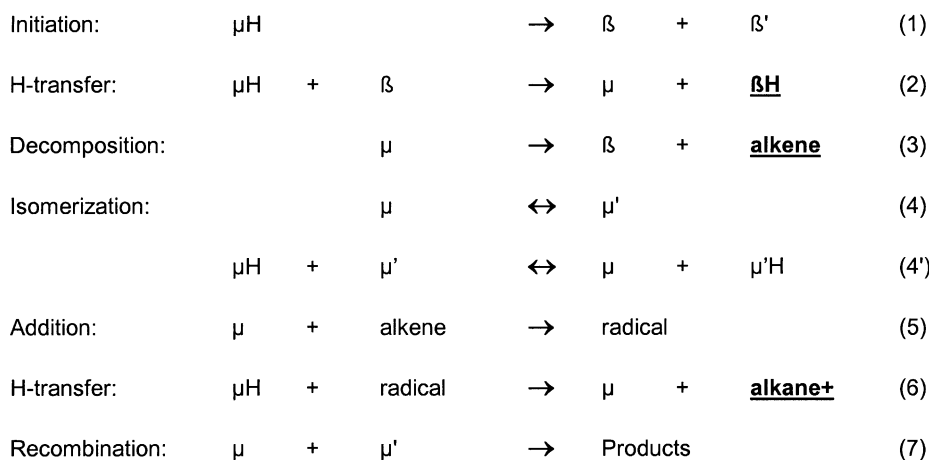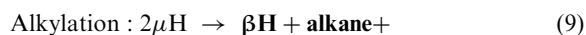| Initiation:	μH			→	ß	+	ß'		(1)
H-transfer:	μH	+	ß	→	μ	+	**ßH**		(2)
Decomposition:			μ	→	ß	+	**alkene**		(3)
Isomerization:			μ	↔	μ'				(4)
	μH	+	μ'	↔	μ	+	μ'H		(4')
Addition:	μ	+	alkene	→	radical				(5)
H-transfer:	μH	+	radical	→	μ	+	**alkane+**		(6)
Recombination:	μ	+	μ'	→	Products				(7)

Fig. 1. Reaction mechanism for the low temperature pyrolysis of alkanes. μH: reactant; β, β′, μ, μ′: radicals. Cracking and alkylation products are shown in bold, underlined (see text).

pyrolysis of an alkane under geochemical conditions can be described by cracking and alkylation stoichiometries (8) and (9), as detailed in Dominé et al. (1998).

$$\text{Cracking}: \mu H \rightarrow \underline{\textbf{βH}} + \underline{\textbf{alkene}} \qquad (8)$$

$$\text{Alkylation}: 2\mu H \rightarrow \underline{\textbf{βH}} + \underline{\textbf{alkane+}} \qquad (9)$$

Isomerization reactions also play a role in products distributions. These can be unimolecular (4) and proceed either by 5- or 6-member ring intermediates (Fig. 2), or bimolecular (4′).

The number of reactions required to describe the pyrolysis of a pure alkane as in Fig. 1 is large, and writing the exhaustive reaction mechanism of the 52 compounds mixture by hand is impossible. We have therefore recently developed (Bounaceur et al., 2002) software that automatically writes free radical reactions for alkane mixtures. This software is an extension of the one initially developed for alkane oxidation by Warth et al., (1998). Most rate constants were taken from compilations (Allara and Shaw, 1980; Baulch et al., 1992; NIST, 1998). When rate constants were not available, they were calculated by analogy with similar reactions, using linear free energy relationships and thermochemical data (see e.g. Bounaceur et al., 2000). Thermochemical data for the species used are also required, as the model runs on the CHEMKIN II software (Kee et al., 1993). When not available in compilations (Gutman, 1990; JANAF, 1971), thermochemical data were calculated. Again, calculations for all species is not possible by hand, and the software THERGAS (Muller et al., 1995) based on the methods of Benson (1976), was used. Additional software, KINGAS, developed at ENSIC (Bloch-Michel, 1995) was used

for the calculation of kinetic data for decomposition and recombination reactions. The reaction mechanisms thus generated have been validated against experimental data with the examples of hexane and tetradecane (Bounaceur et al., 2002), whose mechanisms included 218 and 1700 reactions, respectively. Methods used to reduce the number of reactions by lumping have been detailed in Bounaceur et al. (2001), who illustrated their approach with the example of a mixture consisting of pentane, hexane, heptane, 3-methylpentane and 2,4-dimethylpentane. The reaction mechanism of this 5 alkanes mixture was generated by the software of Bounaceur et al. (2002), and was made up of 7673 reactions, that involved 988 species. Lumping simplified the mechanism to 144 reactions involving 61 species. Bounaceur et al. (2001) also described the methods to calculate the rate constants of the lumped reactions from those of the elementary reactions.

The lumping procedure is briefly summarized below, with two examples where isomeric species and reactions of the same types are regrouped.
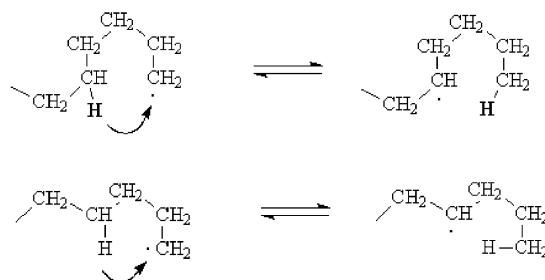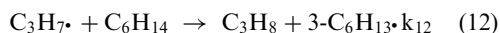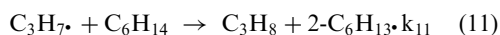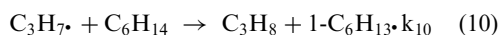

Fig. 2. Examples of 1,5 shift (top) and 1,4 shift (bottom) isomerizations of alkyl radicals.

$$C_3H_7\cdot + C_6H_{14} \rightarrow C_3H_8 + 1\text{-}C_6H_{13}\cdot k_{10} \quad (10)$$

$$C_3H_7\cdot + C_6H_{14} \rightarrow C_3H_8 + 2\text{-}C_6H_{13}\cdot k_{11} \quad (11)$$

$$C_3H_7\cdot + C_6H_{14} \rightarrow C_3H_8 + 3\text{-}C_6H_{13}\cdot k_{12} \quad (12)$$

$$\text{Lump1 } C_3H_7\cdot + C_6H_{14} \rightarrow C_3H_8 + C_6H_{13}\cdot k_{lump1} \quad (13)$$

Lumping by species was done as shown for reactions (10)–(12), and follows the concept detailed by Ranzi et al. (1995) and Tomlin et al. (1997). These three H-transfer reactions all yield propane and isomers of the hexyl radical, that have been lumped in reaction (13) as a single hexyl radical. The rate constant of the lumped reaction is such that the rate of the lumped reaction (13) is equal to the sum of the rates of reactions (10)–(12). Writing the equality of both rate laws yields:

$$k_{lump1} = k_{10} + k_{11} + k_{12} \quad (14)$$

Lumping by reaction types was done as shown for reactions (15)–(19). Five H-transfer reactions of CH_3 to C_5H_{11} radicals on hexane have been regrouped as a single attack of a β radical on hexane, to yield an alkane lighter than hexane. The rate coefficients of these reactions have been assigned the same k_H value, which is a reasonable approximation (Allara and Shaw, 1980). It is clear than lumping reactions results in a loss of information, but the lumping method can be selected to preserve information judged critical, while accepting the loss of information judged secondary.

$$CH_3\cdot + C_6H_{14} \rightarrow CH_4 + C_6H_{13}\cdot k_H \quad (15)$$

$$C_2H_5\cdot + C_6H_{14} \rightarrow C_2H_6 + C_6H_{13}\cdot k_H \quad (16)$$

$$C_3H_7\cdot + C_6H_{14} \rightarrow C_3H_8 + C_6H_{13}\cdot k_H \quad (17)$$

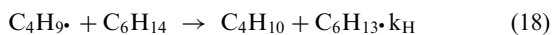$$C_4H_9\cdot + C_6H_{14} \rightarrow C_4H_{10} + C_6H_{13}\cdot k_H \quad (18)$$

$$C_5H_{22}\cdot + C_6H_{14} \rightarrow C_5H_{12} + C_6H_{13}\cdot k_H \quad (19)$$

$$\text{Lump2 } \beta + C_6H_{14} \rightarrow \beta H + C_6H_{13}\cdot k_{lump2} \quad (20)$$
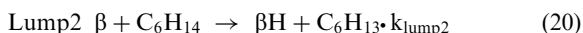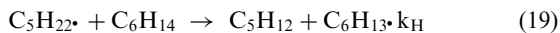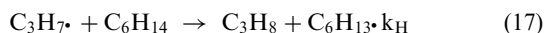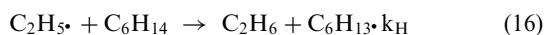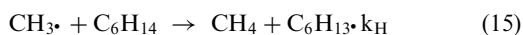
In the case of reactions (15)–(19), the rate coefficient of the lumped reaction (20) will have to obey the same equality of rates as previously. In this case the result is:

$$k_{lump2} = k_H \quad (21)$$

The software used for alkanes is not yet fully automated for non-alkane species. For such compounds, the mechanism of the pure species was written by hand. For example, the mechanism of tetralin has been detailed in Bounaceur et al. (2000). Cross reactions between species such as tetralin and alkanes were written and lumped as described in Bounaceur et al. (in press). The complete mechanism was written by first generating the mechan-

ism of a complex alkane mixture, and then adding incrementally the mechanisms of other chemical structures and the relevant cross reactions. The final mechanism obtained for a mixture of the 52 species of Table 1 has 5200 reactions. Almost all of them are free-radical reactions, but a few retro-ene reactions (Burklé-Vitzhum, 2001) were added to describe the pyrolysis of alkylaromatics.

As shown in Fig. 3, reactions describe the internal exchanges within a given structural family as well as the exchanges between the various types of chemical structures: cyclization of alkanes, formation of aromatics from 6-membered rings, with the involvement of reaction types other than those used for alkanes, such as reverse radical disproportionations, and radical hydrogen transfers (Bounaceur et al., 2000, and references therein), formation of hydroaromatics such as tetralin from the pyrolysis of alkylbenzenes, as observed by Dominé (1991), aromatization of hydroaromatics such as tetralin to form naphthalene, and alkylation of naphthalene to alkyl-naphthalene, thus paving the way for the addition of extra reactions that will yield higher polycyclic aromatic hydrocarbons. The mechanism thus allows the formation of 77 products, detailed in Table 2. In addition to the 52 reactants, these include alkenes, a wide range of alkyl-naphthenes and alkyl-aromatics, butadiene and molecular hydrogen.

3. Results

As written, the 5200 reaction mechanism is valid in the temperature range where reaction types not included
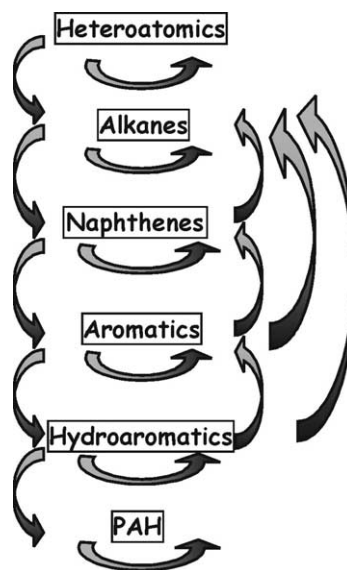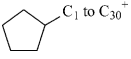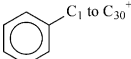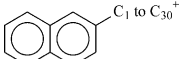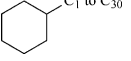

Fig. 3. Exchanges among structural families taken into account in the reaction model.

Table 2
Products other than the reactants of Table 1 formed by the 5200 reaction model

Alkanes	Alkenes	Naphthenes	Aromatics	Naphthalenes	Others
Branched alkanes C_7H_{16} to $C_{29}H_{60}$ regrouped as a single species	C_2H_4	(cyclopentane) C_1 to $C_{30}{}^+$	(benzene) C_1 to $C_{30}{}^+$	(naphthalene) C_1 to $C_{30}{}^+$	(diene) diene
	C_3H_6 C_4H_8 C_5H_{10}				
$C_{30}+$ regrouped as a single species	C_6H_{12} to $C_{29}H_{58}$ regrouped as a single species	(cyclohexane) C_1 to $C_{30}{}^+$			H_2

in the mechanism do not become important. Such reaction types include decomposition of alkyl radicals that yield H atoms, and that become detectable above about 500 °C (Dominé and Enguehard, 1992). Efforts have been made to include all reactions that are expected to have an effect below 450 °C, with the objective to produce a mechanism that can reliably be used at temperatures below 450 °C. This includes the range of geological interest, as well as most of the range used for laboratory experiments. We will first test our model by comparing its predictions with experimental results of the pyrolysis of ELGIN at 372 °C. We will then confront low temperature predictions of our model to geological observations, while making predictions on the maximum temperature of stability of mature oils.

3.1. Validation of the mechanism at 372 °C

A whole oil sample from the Elgin field was pyrolyzed at 372 °C. The Elgin reservoir spreads over 400 m in thickness and the measured reservoir temperatures range from 183 to 192 °C. Corrections are often necessary for measured bottom hole temperatures, and actual temperatures up to 195 °C are likely (Brigaud, 1998). The Elgin field includes two or more distinct reservoirs, resulting in variations in fluid composition. Our ELGIN sample, taken directly at the well head, thus has a composition that is somewhat different from that detailed by Vandenbroucke et al. (1999). They obtained (in mass fraction) 24% CH_4, 6% C_2H_6, and 13% C_3–C_5, while we obtained 39, 8 and 15% respectively. They report 26% in C_6–C_{13} saturates, 6% in C_6–C_{13} aromatics, and 8% in $C_{14}+$ *n*-saturates, while we found 17, 6 and 5%, respectively. Subsequently, we analyzed another ELGIN sample taken separately from our first one and obtained yet another composition, confirming that ELGIN is not homogeneous. In any case, our ELGIN sample appeared more thermally evolved, as it was richer in light compounds and had smaller proportions of heavy ones. We used our first detailed analysis to mimic ELGIN. To transcribe the actual Elgin composition into the 52 species mixture described by our reaction model, we used structural and chemical reactivity analogies to produce the molar composition reported in mixture 7 of Table 3. Molar compositions are always prefered for reactivity considerations. However, organic geochemistry is often concerned with mass balances, and mass compositions of our ELGIN mimic is shown in Table 4. The mass distribution of n-alkanes used is shown in Fig. 4. We did not detect any molecules that could definitely act as accelerators in ELGIN. In particular, we did not find any heteroatoms in aliphatic structures. Our assignment of 0.11 mol% to the disulfide (Table 3) reflects the uncertainty on unidentified molecules, that might have acted as accelerators. This value is most likely an upper limit to the accelerator content of ELGIN.

As mentioned above, ELGIN, like most natural fluids, is not homogeneous throughout its reservoir. Thus, mixture 7 of Table 3 is only an illustration of mature oils. Obviously, the results of many more compositions could be reported. However, changes in the relative proportions of compounds did not change noticeably the conclusions reached in this study on the thermal stability of mature oils.

The liquid and gas fractions of the oil were successively introduced in a stainless steel autoclave, whose pressure was maintained at 500 bars by compression by an inert gas. Experimental durations were between 30 and 1000 h. Analysis was by GC/MS. The time evolution of the mass fraction of several compounds, as observed in the experiments and as calculated by our model, are reported in Fig. 5. The agreement is not perfect for all compounds, although it appears quite satisfactory for some species such as *n*-decane. Excellent agreement is not always expected, because our model inevitably includes simplifications and approximations. The agreement could be improved by adjusting rate constants, as frequently done in geochemical models. However, adjusting rate constant is not part of our

Table 3
Mol% compositions of the seven mixtures used

Species	Mixture number and additives: mol fractions						
	1	2	3	4	5	6	7
	Alkanes only	With tetralin	With Toluene	With disulfide	With 2 alkylaros	With 5 additives	ELGIN
CH_4	18.40	17.6	17.6	17.6	17.6	17.6	75.8
$n\text{-}C_2$ to $n\text{-}C_5$	37.66	40.03	40.03	40.03	40.03	40.03	14.26
$n\text{-}C_6$ to $n\text{-}C_{30}$	17.42	14.81	14.81	14.81	14.81	14.81	2.68
pristane, C_{19}	0.21	0.18	0.18	0.18	0.18	0.18	0.01
phytane, C_{20}	0.21	0.18	0.18	0.18	0.18	0.18	0.01
i-C_4	6.35	5.4	5.4	5.4	5.4	5.4	0.79
i-C_5	5.65	4.8	4.8	4.8	4.8	4.8	0.21
2-MeC_9	2.82	2.4	2.4	2.4	2.4	2.4	0.48
2-MeC_{10}	2.12	1.8	1.8	1.8	1.8	1.8	0.48
3-MeC_{10}	2.12	1.8	1.8	1.8	1.8	1.8	0.48
4-MeC_{10}	2.12	1.8	1.8	1.8	1.8	1.8	0.48
2-MeC_{11}	2.12	1.8	1.8	1.8	1.8	1.8	0.48
Propyl-c-C_5	1.41	1.2	1.2	1.2	1.2	1.2	0.93
Propyl-c-C_6	1.41	1.2	1.2	1.2	1.2	1.2	0.89
Tetralin	0	5.0	0	0	0	1	0.25
Toluene	0	0	5.0	0	0	1	0.90
Butylbenzene	0	0	0	0	2.5	1	0.25
decylbenzene	0	0	0	0	2.5	1	0.52
di-iC_3-diS	0	0	0	5.0	0	1	0.11

Table 4
Mass% compositions of the seven mixtures used

| Species	Mixture number and additives: mass fractions						
	1	2	3	4	5	6	7
	Alkanes only	With tetralin	With Toluene	With disulfide	With 2 alkylaros	With 5 additives	ELGIN
CH_4	4.06	3.74	3.99	3.83	3.77	3.85	38.85
$n\text{-}C_2$ to $n\text{-}C_5$	23.93	25.01	26.68	25.63	25.22	25.76	17.62
$n\text{-}C_6$ to $n\text{-}C_{30}$	30.91	25.28	26.97	25.91	25.32	25.85	13.39
pristane, C_{19}	0.78	0.64	0.68	0.66	0.65	0.66	0.07
phytane, C_{20}	0.83	0.67	0.72	0.69	0.68	0.69	0.10
i-C_4	5.09	4.16	4.44	4.26	4.19	4.28	0.89
i-C_5	5.62	4.59	4.89	4.70	4.63	4.72	1.11
2-MeC_9	5.54	4.52	4.83	4.64	4.56	4.66	2.18
2-MeC_{10}	4.57	3.73	3.98	3.82	3.76	3.84	2.40
3-MeC_{10}	4.57	3.73	3.98	3.82	3.76	3.84	2.40
4-MeC_{10}	4.57	3.73	3.98	3.82	3.76	3.84	3.95
2-MeC_{11}	4.98	4.06	4.33	4.16	4.10	4.18	1.12
Propyl-c-C_5	2.19	1.85	1.90	1.82	1.80	1.84	3.35
Propyl-c-C_6	2.46	2.08	2.14	2.05	2.02	2.07	3.60
Tetralin	0	9.07	0	0	0	1.80	1.05
Toluene	0	0	6.50	0	0	1.26	2.65
Butylbenzene	0	0	0	0	4.48	1.83	1.09
decylbenzene	0	0	0	0	7.30	2.98	3.66
di-iC_3-diS	0	0	0	10.18	0	2.05	0.50
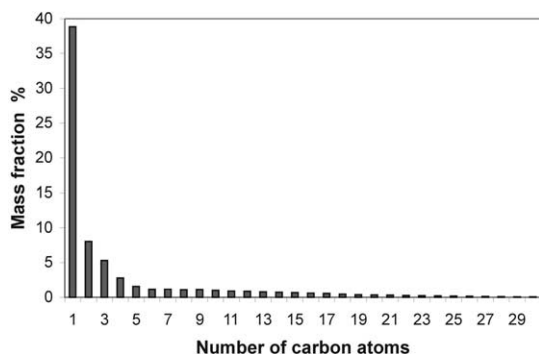
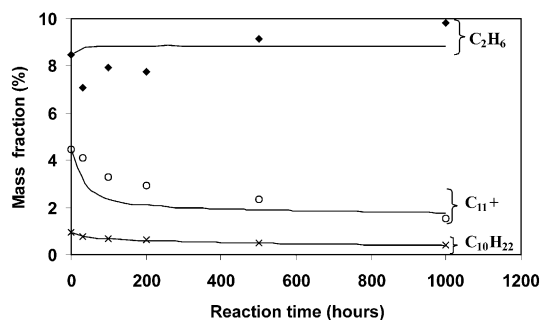Fig. 4. Mass distribution of n-alkanes used to model ELGIN oil.

Fig. 5. Examples of experimental results and model calculations for the pyrolysis of Elgin fluid at 372 °C. Ethane (top), n-decane (bottom), and the sum of $C_{11}+$ hydrocarbons (middle) are shown.

approach. On the contrary, we use rate constants of elementary reactions that have been directly measured or calculated using well established methods, and there is no physical basis for changing them. The purpose of the present work is to elaborate a model that will be valid for all oil compositions, and not just for ELGIN. Thus, optimizing model output for a limited number of oils is not considered as a valid approach. Improvements in model output should instead come from an increased number of reactions and from a larger number of species in the model mixture. Experimental error can also contribute to the small differences between experiment and model. Indeed, both the reacting oil and reaction products consisted of gaseous and liquid phases, and phase mixing and separation are an extra source of error.

Another validation of our model has been reported by Bounaceur (2001), who simulated with this same reaction scheme the experimental pyrolysis of Pematang oil at 450 °C reported by Ungerer et al. (1988). The transcription of Pematang oil composition in terms of our 52 species requires lengthy explanations and will not be reported here, and the interested reader is referred to Bounaceur (2001) for details. The agreement between

experiments and model was good for all compound classes used by Ungerer et al., and was very good for the C_2–C_5 and $C_{13}+$ fractions.

Given these considerations, we conclude that our model reproduces in a satisfactory manner the pyrolysis of oils under laboratory conditions. Although this is no definite proof of its universality, it does contribute to its validation, and we will now investigate its predictions at geological temperatures.

3.2. Simulations at geological temperatures

The main purpose of this section is to attempt to determine the thermal stability of mature oils, and to investigate the effect of oil composition on thermal stability. We will thus submit mixtures of selected composition to a thermal history typical of a mature oil (e.g. Vandenbroucke et al., 1999): initial temperature at 160 °C, and heating at 1.5 °C per million years (Ma). The initial temperature was chosen as 160 °C because model runs under 160 °C showed no detectable thermal evolution over geological time scales, in agreement with earlier modeling work of Dominé et al. (1990, 1998) on hexane. Our strategy will be to first model the evolution of a mixture made up mostly of alkanes, and then to compare its thermal stability to mixtures where other types of species have been added. This will allow the understanding of the inhibiting or accelerating effects of other types of species in the pyrolysis of alkanes.

The initial alkane mixture chosen, somewhat arbitrarily, attempts to resemble the distribution of alkanes in oils. Its molar and mass compositions are shown in Tables 3 and 4 (mixture 1). On a molar basis, CH_4 is the most important species: 18.4% of mixture 1. Mass fractions are commonly used in geochemistry, and the mass distribution of n-alkanes is therefore shown in Fig. 6. The thermal transformations of this mixture were modeled to determine its stability. Defining precisely the "stability" of this mixture conveys an arbitrary character. Because the economic value of an oil is to some extent determined by the fraction of hydrocarbons with a moderate molecular mass, we chose here to define stability as the half-life of the C_6–C_{13} n-alkane fraction. Thus, *the maximum temperature of stability of a given mixture will be when the initial mass fraction of C_6–C_{13} n-alkanes will have been reduced by half*. Obviously, other definitions with a similar arbitrary character could be adopted. Note also that our results will be determined for the heating rate of 1.5 °C/Ma specified above, and that the stabilities obtained also slightly depend on heating rates.

The evolution of the mass fraction of the C_6–C_{13} n-alkanes of mixture 1 is shown in Fig. 7. This shows that, according to our definition of stability, the alkane mixture is stable up to 214 °C, as reported in Table 5. With added tetralin (mixture 2), a known inhibitor of alkane pyrolysis (Khorasheh and Gray, 1993; Bounaceur
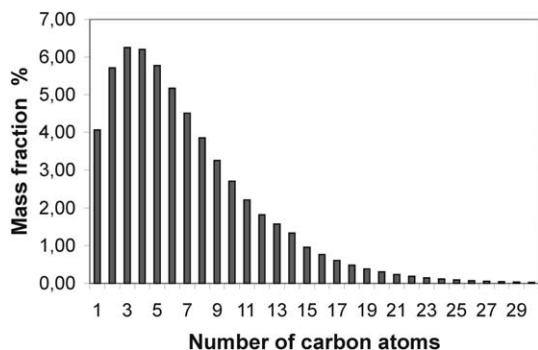
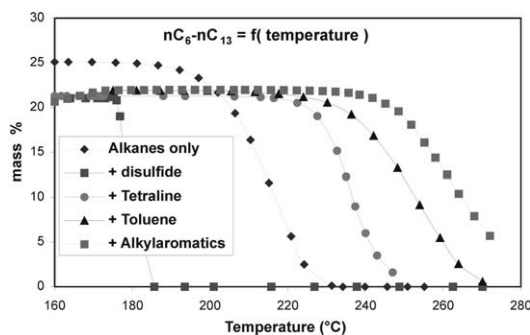Fig. 6. Mass distribution of n-alkanes used to model the first six compositions of Table 3.

Fig. 7. Evolution of the mass fraction of the n-C_6 to n-C_{13} fraction of the first 5 mixtures of Table 3, subjected to a heating rate of 1.5 °C per Ma.

et al., in press a), Fig. 7 shows that the destruction of the n-C_6–n-C_{13} fraction is significantly delayed, and the stability of mixture 2 is 237 °C (Table 5). Toluene is an even more efficient inhibitor, and Fig. 7 shows that the addition of 5 mole% toluene (mixture 3) stabilizes the alkane mixture even further, to 250 °C (Table 5). Alkylaromatics provide yet an extra increase in stability, as the addition of 2.5 mol% each of butyl- and decyl-benzene increases the stability to 264 °C (Fig. 7 and Table 5). However, the addition of 5 mol% disulfide

(mixture 4) strongly accelerates the destruction of alkanes, as the stability is then greatly reduced to 180 °C.

Hence the potential role of reaction accelerators appears to be about as strong and opposite to that of reaction inhibitors. It is crucial to determine which one of both these effects will be predominant in a complex mixture. Fig. 8 shows that the 5 additives added together (mixture 6) lead to an enhanced stability of the alkane mixture: 233 °C vs. 214 without any additive (Table 5), showing that the inhibiting effect is preponderant. The fact that there is only 1% accelerator and 4% inhibitor is not really crucial, as numerous other runs showed that the inhibiting effect always predominates, even with much more accelerator than inhibitor.

A final run was performed with composition 7, that mimics ELGIN. Fig. 8 and Table 5 show that ELGIN is stable up to 237 °C. Fig. 9 shows the evolution of its composition with temperature during our model runs. Our model does not actually describe coke formation. In this Figure, coke is represented by heavy aromatics, that are coke precursors: alkyl-substituted naphthalenes and $C_{14}+$ alkylbenzenes, formed by the addition of an alkyl radical on decylbenzene. Fig. 9 shows that the composition of the Elgin fluid does not change much until about 220 °C, but extensive changes have taken place at 240 °C. This is also quite apparent if we consider the gas to oil ratio (G.O.R.), shown in Fig. 10. Its initial value is 1440. At 200 °C, it has increased only to 1590. It remains moderate at 220 °C: 1900, but climbs to 4550 at 240 °C.

4. Discussion

Our model shows that the composition of the mixture has a critical impact on its thermal stability. Tetralin has a stabilizing effect, as expected from the literature (Khorasheh and Gray, 1993; Bounaceur et al., in press). Toluene is even more efficient to stabilize alkanes. This is because toluene cannot be involved in secondary initiation reactions by reverse radical disproportionation, while tetralin can (Bounaceur et al., 2000). Thus, tetralin does have an accelerating character, as it provides extra facile bimolecular initiations, while its inhibiting

Table 5
Maximum temperatures of stability of the 7 mixtures of Table 3 subjected to a heating rate of 1.5 °C/Ma (see text)

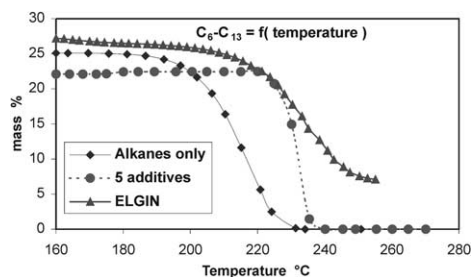| Species	Mixture number and additives						
	1	2	3	4	5	6	7
	Alkanes only	With tetralin	With Toluene	With disulfide	With 2 alkylaros	With 5 additives	ELGIN
Temperature of stability, °C	214	237	250	180	264	233	237

Fig. 8. Evolution of the mass fraction of the n-C$_6$ to n-C$_{13}$ fraction of mixtures 1, 6 and 7 of Table 3, subjected to a heating rate of 1.5 °C par Ma.
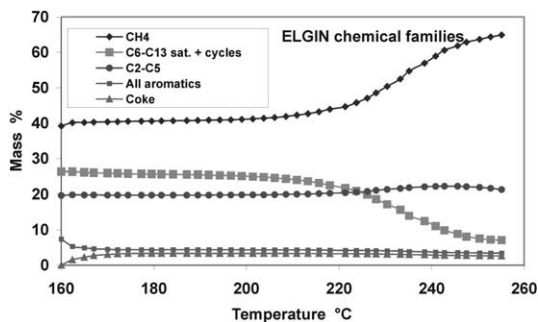

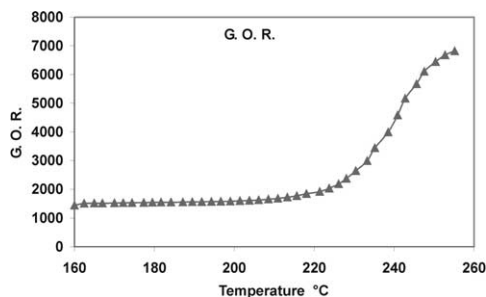Fig. 9. Evolution of the distribution of chemical families during the heating of ELGIN oil (composition 7 of Table 3), at a rate of 1.5 °C par Ma.

Fig. 10. Evolution of the gas to oil ratio of ELGIN oil subjected to a heating rate of 1.5 °C per Ma.

effect is caused by the accumulation of the resonance-stabilized 1-tetralyl radical (Bounaceur et al., 2000) that increases the termination rate. Toluene, on the contrary, is a pure inhibitor because of the accumulation of the resonance-stabilized benzyl radical.

It may seem surprising that the addition of two alkylaromatics results in a stronger inhibiting effect than when toluene is added. Indeed, alkylaromatics do have an accelerating effect, as the formation of benzyl and alkyl radicals is facilitated by the weakness of the β–C–C bond of the alkyl bond (Dominé et al., 1990; Dominé, 1991). The inhibiting effect of alkylaromatics is also caused by the accumulation of benzyl radicals. A

careful look at the model results show that pyrolysing alkylaromatics produces toluene continuously, via retro-ene reactions. Thus, once thermal transformations do start, the mixture with toluene sees its toluene content decrease fast, while with alkylaromatics, a continuous supply of toluene exists. Since toluene is the only pure inhibitor that we have found amongst simple hydrocarbons, the mixture with the higher toluene concentration will be more stable. At 240 °C, mixture 5 has more toluene than mixture 3, and it is thus more stable.

Because di-isopropyl-disulfide readily forms radicals by scission of the weak S–S bond (Benson, 1976), it has a strong accelerating effect. However, disulfides do not exist in mature oils (Hughes, 1984). In fact, it is likely that efficient accelerators are not present in mature oils, as their low thermal stability does not allow them to survive at high temperatures. A legitimate question is then: is there any strong accelerating effect in mature petroleum? Further detailed analytical work is needed to answer this question, but from our present understanding of accelerating and inhibiting effects in oils, we are inclined to suggest that the answer is: no.

If this is indeed the case, then the more reliable estimate of the stability of petroleum that we can make from the present results will be by considering the data obtained with mixtures 2, 3, and 5. It thus appears likely, from this work, that the stability of petroleum will depend on its composition, and will be in the 240–260 °C temperature range. This range is significantly higher than that given by most geochemical models that use the Tissot approach. Even fairly recently, Dieckmann et al. (1998) predicted with that approach that oil generated from Toarcian shales would start decomposing at 150 °C and would be severely degraded at 210 °C.

5. Summary and conclusion

We have proposed a new modeling approach based on free-radical reactions. This approach is not empirical, as it includes all the types of free-radical reactions that can be reasonably expected to take place in the pyrolysis of hydrocarbons under 450 °C. It also contains molecular reactions such as retro-ene reactions that produce toluene from the pyrolysis of alkylaromatics (Burklé-Vitzthum, 2001). The rate constants of elementary processes used in the present model have been either individually measured in laboratory experiments, or estimated using methods widely used in the chemical kinetics community.

By lumping reaction types and species with similar structures, we were able to limit the number of reactions to 5200, and model the pyrolysis of a mixture of 52 reactants, whose transformations are described by the formation of 77 species. Obviously, not all species present in mature oils can be described individually, and this

would have little interest anyway. The limited number of species used does however introduce uncertainties, and the main one is probably the lack of detailed representation of macromolecules: resins and asphaltenes. Fortunately, such macromolecules are not abundant in mature oils. A possible perturbing effect to expect from them would be to accelerate pyrolysis. It is difficult to imagine, however, that they could contain species with an accelerating effect stronger than the strongest accelerator used here, di-iso-propyl-disulfide. We are thus reasonably confident that the results obtained here with our representation of ELGIN yields a lower limit of stability of mature oils.

This model can readily be used for any mature oil. Once validated, as described above and in more detail in Bounaceur (2001), it needs no calibration, as rate constants are not adjustable. This is one major change from previous models, that required calibration for the case for which its use was intended. The only input parameters are the oil composition and its thermal history. Thus the only exercise will be to transform a detailed oil analysis into mole fractions of the 52 reactants selected in Table 1. This should be done using analogies in structure, mass, and kinetic behavior.

The main conclusion from this work is that oils are stable at much higher temperatures than previously thought, and can be expected to be found at temperatures as high as 240–260 °C, depending on their composition. This has considerable economic and scientific impact. Because heavy hydrocarbons escape from rock layers with greater difficulty than CH_4 or light alkanes, the residence time of hydrocarbons in the earth crust will be increased. This will also change the expected composition of fluids in contact with minerals in sedimentary basins. While CH_4 is generally thought to be dissolved in water in contact with organic materials, this study suggests that heavier hydrocarbons will be more present than initially thought. This will modify water activity and shift mineral equilibria, as already mentioned by Dominé (1991).

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