

Chapter 1 Exercises

1. *What is the difference between crude oil and petroleum?*

Although both words have a range of meanings and are sometimes used interchangeably, most technical sources consider petroleum to be a broader classification of materials. Crude oil is a type of petroleum that exists in liquid phase in natural underground reservoirs AND remains liquid at atmospheric pressure after passing through surface separating facilities. In other words, crude oil is a component of petroleum. Petroleum includes crude oil and natural gas liquids (e.g., liquid propane). The US EIA includes biofuels and refined products as petroleum but specifically excludes natural gas, while Hunt includes natural gas as petroleum. Crude oils produced by thermal means from coal, kerogen, or natural gas are often called synthetic crude oils, or syncrude.

2. *The following questions address the usage of various energy forms:*

a. *According to the most recent statistics, what is the largest energy source in the world and is it the same in the United States?*

In 2015, the largest energy source in the world is petroleum, and it is also the largest energy source in the United States.

b. *What notable difference is there between the importance of coal in the United States and the world?*

In the United States, coal is third in importance, behind natural gas, and its use is dropping rapidly. Coal is still the second largest source in the world, although it appears to have peaked and may be overtaken by natural gas in a few years.

c. *Do you expect that natural gas will overtake petroleum in the United States as an energy source? Why or why not, and if so, when?*

The answer to this question involves predicting the future, so your answer should be graded on the quality of the data and logic used in your prediction.

3. *What is the most abundant maceral in coal, and what is its source?*

Vitrinite is the most common maceral in coal (more specifically, in humic coals, which are the most abundant type of coal) and it comes from the woody tissue in land plants.

4. *Are all coals predominantly humic?*

No, boghead and cannel coals are predominantly sapropelic. Most coals are predominantly humic, but most is not the same as all.

5. *What maceral group is sapropelic, and what is its most important feature with respect to fossil fuels?*

Liptinite is the general maceral type for sapropelic matter, and its high hydrogen and low oxygen content relative to vitrinite means that oil is its primary product during catagenesis. Other properties may be important for specific purposes, but its generative potential is the most important.

6. *What are three differences between the Gray-King and Modified Fischer Assay?*

There are more than three, depending on how the differences are grouped.

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- The Gray-King Assay is primarily used to assess the suitability of coal to make coke, while Modified Fischer Assay is used to assess oil and gas potential from oil shales.
- The Gray-King Assay uses a glass (fused silica) tube and the Modified Fischer Assay uses an aluminum retort.
- The Gray-King Assay uses 20 g vs. 100 g for the Modified Fischer Assay.
- The Gray-King Assay heats the sample as fast as the furnace can heat, while the Modified Fischer Assay heats the sample at a programmed rate of ~ 12 °C/min.
- The Gray-King Assay has a higher final temperature, ranging from 550 to 900 °C, while the Modified Fischer Assay reaches only 500 °C.

7. What national research organization pioneered the use of Rock-Eval characterization?

The Institut Français du Pétrole (IFP)

8. An organic-rich rock has $S_1=15$ mg/g rock, $S_2=80$ mg/g rock, and $TOC=9.5$ wt%. What are its HI and PI? What kerogen type is it?

$HI = S_2/TOC$ in mg/g, so $HI = 80 \text{ mg/g rock} / 0.095 \text{ g TOC/g rock} = 842 \text{ mg/g TOC}$

$PI = S_1/(S_1+S_2) = 15/(15+80) = 0.16$

It is an immature Type I kerogen.

9. Give two different definitions of pyrobitumen used by different research communities.

- For oil shale retorting, numerous workers use the term to describe the initial soluble heavy materials formed during pyrolysis.
- For petroleum geochemists, pyrobitumen is the solid, insoluble material remaining after liquid bitumen is converted to semi-coke during catagenesis.
- A third archaic definition constructed before modern organic geochemistry is any insoluble preserved organic material, which includes kerogen and coal, and that definition should be abandoned.

10. What coal rank has the largest concentration of extractable organic matter?

Bituminous. The extractability depends on solvent and conditions, but as shown in Figure 1.8, the maximum extractability is at about 86% carbon, dry and ash-free. This falls in the medium-volatile bituminous range, which corresponds to the oil window for sapropelic kerogen.

Chapter 2 Exercises

1. *What can and cannot be learned about global chemical kinetic parameters from transition-state theory?*

Transition-state theory introduces the concepts that a hypothetical species exists at the top of the energy barrier for a chemical reaction and that a component of its decomposition rate constant is a molecular vibrational frequency, which is order $1 \times 10^{13} \text{ s}^{-1}$. So that is qualitative guidance for unimolecular dissociation reactions. However, complex reactions also contain entropic terms and collision frequencies for complex reactions, so the qualitative guidance becomes even less quantitative. Furthermore, the apparent activation energy of chain reactions is often approximated by the activation energy of the propagation reaction plus half the difference between the initiation and termination reactions, which does not relate directly to transition-state theory. Consequently, any invocation of transition state theory for global chemical kinetics should be viewed with considerable caution. Computational advances have enabled mechanistic calculations for complex reaction networks in which each fundamental reaction is governed by transition-state theory, and that kind of work merits the invocation of transition-state theory for its conclusions.

2. *Explain one example for which the approximation $d\alpha/dt = k(T)f(\alpha)$ is not valid.*

This equation presumes that the same set of reactions occur at each conversion independent of temperature. The simplest example of when this approximation fails is for competitive reactions with different activation energies. Here, the reaction pathway has a branch point, and the weighting of the two pathways after the branch point depends upon temperature. Consequently, the same reactions are not sampled after the branch at different temperatures.

3. *Show that the formulas for a pseudo nth-order reaction in Table 2.1 are equivalent to Eq. 11 in Burnham and Braun, Energy & Fuels 13, 1-22 (1999).*

The integral form of the pseudo-nth-order reaction in Table 2.1 is

$$g(\alpha) = \frac{1}{n-1} [(1-\alpha)^{(1-n)} - 1] = \int_0^t k(t) dt$$

Burnham and Braun use fraction remaining rather than fraction reacted, so substituting $x=1-\alpha$,

$$\frac{1}{n-1} [x^{(1-n)} - 1] = \int_0^t k(t) dt$$

A little algebra gives

$$x^{(1-n)} = 1 + (n-1) \int_0^t k(t) dt$$

and then

$$x = \left[1 - (n-1) \int_0^t k(t) dt \right]^{1/(1-n)},$$

which is eq. 11 of Burnham and Braun.

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4. Kinetic T_{max} values of a first-order reaction are 434.5, 460.6, and 488.6 °C at constant heating rates of 2, 8, and 32 °C/min. Write a simple spreadsheet or other program for Kissinger's method and calculate A and E .

The program is a simple linear regression of Kissinger's equation

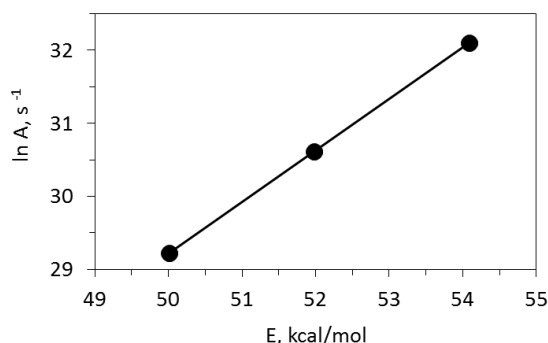
$$\ln(\beta/T_{max}^2) = \ln(AR/E) - E/RT_{max}$$

where β is in °C/s and T is in Kelvin. The slope is E/R , and then A is calculated from the intercept using that E/R . The fitted values are $A = 1.97 \times 10^{13} \text{ s}^{-1}$ and $E = 51.98 \text{ kcal/mol}$, which are not exactly equal to the values used to generate the T_{max} values due to round-off errors. However, the differences are insignificant from a practical perspective and are more accurate than can be achieved with real data.

5. If there is a measurement error for T_{max} of +1 °C at 32 °C/min and -1 °C at 2 °C/min, what are the resulting A and E ? Now repeat the calculation with the signs of the temperature errors reversed. Plot the $\ln(A)$ versus E for these two pairs along with the pair from problem 4. What does it mean?

$4.94 \times 10^{12} \text{ s}^{-1}$ and $E = 50.01 \text{ kcal/mol}$;

$8.70 \times 10^{13} \text{ s}^{-1}$ and $E = 54.09 \text{ kcal/mol}$



The lesson is that measurement errors can cause a compensation effect between A and E that has no mechanistic meaning.

6. Write a spreadsheet or other program to calculate the reaction rate and fraction reacted of a first-order reaction for (at least) a constant heating rate. Justify your choice of integration method. Generate simulated data for three parallel reactions with $A = 1 \times 10^{13} \text{ s}^{-1}$, $E = 49, 51, \text{ and } 53 \text{ kcal/mol}$, and weighting factors of 0.2, 0.5, and 0.3, respectively, at 1, 5, and 25 °C/min. What are the temperatures for 50% conversion at the three heating rates?

416.8, 446.2, and 478.3 °C

7. For the simulated data from problem 5, what is the full width at half height (FWHH) of the reaction rate profile at 5 °C/min? What is the FWHH of the reaction rate profile for the principal reaction channel (51 kcal/mol) at the same heating rate? From the ratio of the two profile widths and the simpler equation in Table 2.3, what is an estimate for the Gaussian E -distribution parameter, σ .

71.1 °C; 47.5 °C; $\rho = 1.50$; $\sigma = 2.86\% \text{ of } E_0$

The nonlinear regression value of σ determined by Kinetics2015 is 2.91% of E_0 .

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8. For the simulated data from problem 5, use Friedman's method to calculate the instantaneous first-order A and E values at 10%, 30%, 50%, 70%, and 90% conversion.

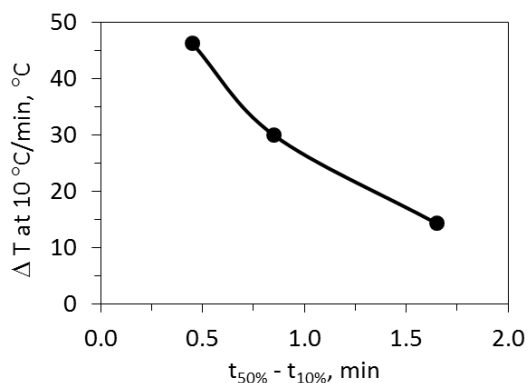
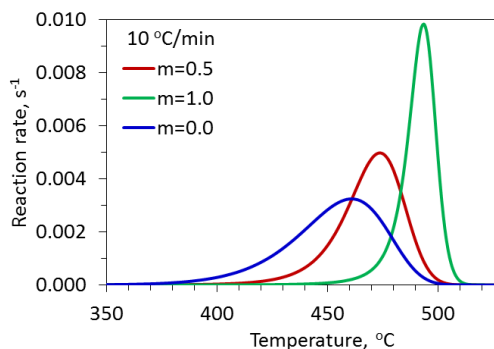
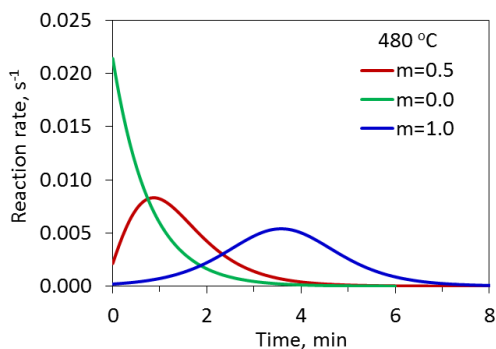
	A, s^{-1}	$E, \text{kcal/mol}$
10%	7.06e12	50.20
30%	1.01e13	51.11
50%	1.24e13	51.87
70%	1.22e13	52.30
90%	1.71e13	53.60

9. What is the purpose of the parameter q in the extended Prout-Tompkins model (eqn. 2.38) and what is the approximation associated with it having a constant value.

The purpose of q is to provide a non-zero reaction rate at $t=0$ for numerical integration of the reaction rate over time. Having q be independent of temperature is equivalent to having the same activation energy for initiation and propagation (or nucleation and growth) reactions.

10. Write a spreadsheet or other program to calculate the reaction rate and fraction reacted for the extended Prout-Tompkins model (eqn. 2.38) for an arbitrary thermal history. Plot the reaction rate curves at 480 °C and 10 °C/min for $A=1 \times 10^{14} s^{-1}$, $E=54$, $q=0.99$, and $m=0.0, 0.5$, and 1.0 . Plot the isothermal times between 10 and 50% conversion versus the profile full widths at half height for $m=0.0, 0.5$ and 1.0 . Why does the curve have a negative slope?

Reaction rates calculated using Kinetics2015



As m increases, the reaction takes longer to get going. This increases the 10-50% conversion time interval at constant temperature. But the delay at a constant heating rate means that the temperature has increased by the time the reaction gets going, so the reaction occurs over a narrower time-temperature interval.

Chapter 3 Exercises

1. *Is kerogen a polymer? Why or why not?*

Kerogen is definitely macromolecular, but whether it is a polymer is debatable, even though it is often called a geopolymer. One view is that it does not follow the restrictive definition of being made from repeating units, so it should not be considered to be a polymer. It is certainly not like polystyrene or polypropylene. However, that view is far too restrictive, in my opinion. First, proteins are widely considered to be polymers due to the repeating polypeptide linkage, but the side chains are variable. Similarly, DNA is a polynucleotide with variable side chains. Second, synthetic polymers often contain random blocks of different molecules to tailor particular properties. Third, some well-preserved algal kerogens have chemical structures and pyrolysis characteristics very similar to synthetic polymers. So kerogen stretches but does not break the definition of polymer. However, calling kerogen a geomacromolecule is more rigorously correct.

2. *Order the three main kerogen types in order of increasing aromaticity.*

Type I (algal), Type II (planktonic), and Type III (humic).

The aromaticity increases as H/C ratio decreases from Type I to Type III. Caution: although this definitional scheme is widely used, it is also widely understood to be an oversimplification of the diversity of kerogens due to variations in source input and depositional conditions.

3. *Does the aliphatic or aromatic portion of kerogen yield more oil, and why?*

The aliphatic portion yields more oil, because saturated hydrocarbon chains tend to form the types of molecules in oil and aromatic structures tend to form coke.

4. *What is the primary type of bond determining the three-dimensional structure of low-rank humic coal?*

Hydrogen bonds, because low-rank coals contain lots of hydroxyl groups, and the three-dimensional structure is formed by folding of molecular chains into a structure stabilized by weaker bonds.

5. *What are the two main characteristics solvent swelling studies probe?*

- (1) Average solubility parameter from which solvents cause the most amount of swelling.
- (2) Molecular distance between crosslinks from the amount of swelling at optimal solubility parameter.

6. *How does asphaltene structure relate to kerogen structure? What is a typical molecular weight?*

Asphaltenes are considered to be subunits of kerogen formed during the initial decomposition stages. The most commonly accepted average molecular weight is 700 daltons (amu), which is roughly C_{50} and larger than any molecule you will find in shale oil or crude oil distillates because it is too large to be volatile.

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Single Core: atomic force and scanning tunneling microscopy of single asphaltene molecules have observed only single cores.

Archipelago: pyrolysis of asphaltenes often yields alkylated benzenes and naphthalenes that could not have been formed by the breakdown of large polyaromatic rings.

8. Does the Rock-Eval T_{max} always represent pyrolysis? Why or why not?

No, low volatility molecules evolve during the S2 peak simply by evaporation rather pyrolysis, and for some materials (e.g., bitumen sands and mature source rocks) the evaporation of these low volatility components can perturb or even dominate the T_{max} value.

9. What are the weakest and strongest covalent bonds thought to occur in kerogen structures?

The weakest covalent bonds involve sigma sulfur bonds and the aliphatic side of aliphatic-aromatic ether bonds. The strongest covalent bonds (other than aromatic bonds within rings) are ether and alkyl bonds to the aromatic rings.

10. Why does a linear macromolecular structure lead to a sigmoidal reaction relation for volatile product generation?

The breaking of a single bond by random scission is unlikely to form a fragment small enough to be volatile. As more bonds are broken, the likelihood of forming a volatile fragment increases, so the formation of volatiles accelerates with conversion. In contrast, the breaking of a single bond in a highly branched structure will likely lead to a volatile fragment, meaning that the fastest rate of volatile generation is at the start.

Chapter 4 Exercises

1. *What is an appropriate sample size for a kinetics experiment involving a rapidly heated sample, why is it important, and how is it determined?*

A good estimate for a sample size is less than $50 \text{ mg} \cdot ^\circ\text{C}/\text{min}$. Scaling with heating rate keeps the thermal transients and detector response in the same range. It is important not to have too large of a sample or it will contain thermal gradients that invalidate the sample temperature measurement and the resulting chemical kinetic parameters. This general guideline assumes a total heat load typical of an organic polymer and a spherical sample. The tolerable amount might be greater or less depending on the heat capacity and enthalpy of reaction, the geometry of the sample, and the thermal conductivity of the surrounding carrier gas. One can check whether temperature gradients are a problem by measuring the reaction rate as a function of sample size at one heating rate and then scaling the others as appropriate.

2. *What is the proper definition of a mathematical convolution, and what is its practical impact on chemical kinetic measurements and analysis?*

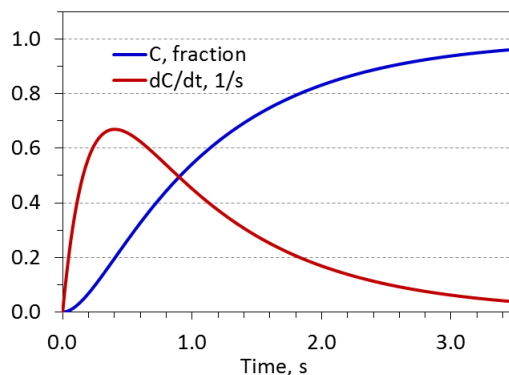
The proper definition of a mathematical convolution is given in eqn. 4.1. It appears in the convolution of the reaction rate over a continuous energy distribution for some reaction models. For measurements, the true time dependence of the chemical reaction signal can be broadened by convolution over temperature distribution across the sample or convolution over diffusional and convective dispersion of a product on its way to the detector. This broadening of the signal can introduce errors into the derived chemical reaction parameters, especially if the gradients and dispersion are a function of temperature or heating rate. Its effect can be removed through mathematical means if a transfer function can be measured.

3. *For the mechanism $A \rightarrow B \rightarrow C$, the amount of C versus time is $[k_2(1-\exp(-k_1t)) - k_1(1-\exp(-k_2t))]/(k_2 - k_1)$.*

a. *Derive an equation for dC/dt .*

$$\frac{dC}{dt} = \frac{k_1 k_2}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

b. *Plot C and dC/dt as a function of t for $k_1=5$ and $k_2=1$. For what value of t is dC/dt at its maximum?*

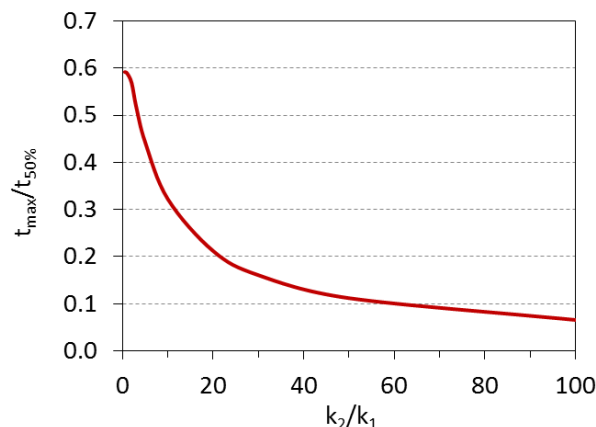


- c. *If k_1 is infinite, what is $t_{50\%}$ (50% conversion to C)? What value of k_2/k_1 is required to have less than 5% error in $t_{50\%}$?*

0.693 s, 30

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- d. Plot the ratio of the times for maximum generation rate and 50% conversion as a function of k_2/k_1 . From 1.001 to 100. What value of k_2/k_1 is required before that ratio is less than 0.10? ~60



- e. What are the implications of these calculations regarding statements that the reaction mechanism is sequential but the appearance of C is first-order?

For the appearance of C to appear first order, the conversion of A to B must be tens of times faster than the conversion of B to C, and depending on the degree of accuracy desired, about 100× faster.

4. What is the approximate ratio of reaction rates for devolatilization of low and high rank coals?
~100x

5. These questions deal with the relationship between variations in T_{\max} and variations in A and E.

- a. What 50 °C interval spans the range of immature kerogen Rock-Eval T_{\max} values?

395-445 °C

- b. What is the difference in °C between Rock-Eval T_{\max} and the true T_{\max} ?

36-38 °C

- c. For a constant frequency factor of $1 \times 10^{14} \text{ s}^{-1}$, what is the corresponding range of activation energy?

50.6 to 54.3 kcal/mol

- d. For a mean activation energy of 54 kcal/mol, what is the corresponding range of frequency factors?

1.25×10^{15} to $8.0 \times 10^{13} \text{ s}^{-1}$

6. What hundred-fold range of A encompasses most immature kerogen samples?

$1 \times 10^{13} \text{ s}^{-1}$ to $1 \times 10^{15} \text{ s}^{-1}$

7. Why do some kerogens require a sigmoidal reaction model?

Some well-preserved algal kerogens have a structure more linear than branched, so multiple bonds must be broken before products are formed that are small enough to be volatile. The character is similar to what is observed for linear synthetic polymers.

8. What is the mathematical form commonly used to relate frequency factor to activation energy, and how does it relate to the changes one might expect in those parameters with maturity?

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$\ln A = a + bE$. When using the common assumption of the same frequency factor for all reaction channels, one would expect the apparent frequency factor to increase with maturity as the remaining reaction channels dominating the reactivity increase due to faster depletion of the lower energy reaction channels.

9. *Why do slower heating rates cause longer liquid-phase residence times, and what is the practical consequence of that residence time? What does that say about the relative activation energies of oil vaporization and coking?*

Slower heating rates cause liquid products to be generated at lower temperatures because of the longer residence time at any given temperature. Liquid-phase residence time is inversely related to vapor pressure, which decreases with temperature. Consequently, unstable oil components have longer times to undergo retrograde coking reactions. As temperature increases, both the oil coking rate constant and vapor pressure increase with temperature. If the residence time decreases more than the coking rate constant increases, the amount of coking will also decrease. Because coking decreases at the higher temperatures, the effective activation energy for coking must be smaller than for vaporization.

10. *These questions deal with gas generation.*

- a. *What are approximate values for the gas/oil ratio during open pyrolysis for Types I, II, and III kerogen? See the last section in Chapter 4.*

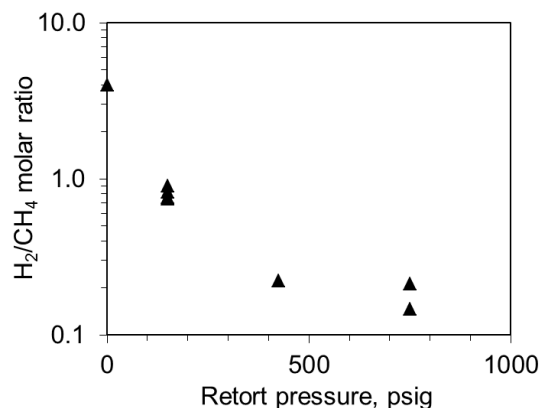
	Burnham		Behar		average
Type I	0.12		0.11		0.11
Type II	0.14	0.20	0.13	0.14	0.16
Type III			0.39	0.37	0.38

- b. *What are the two primary gases emitted from kerogen during open-system pyrolysis after oil potential is depleted?*

CH_4 and H_2

- c. *Do you expect the ratio of H_2 to CH_4 is the same in open-system pyrolysis and nature? Why or why not?*

No, because the H_2 will react at high pressures with other organics to saturate alkenes and to form methane. Here are results from Burnham and McConaghy (2014).



Chapter 5 Exercises

1. *When coal melts during pyrolysis, bubbles form. How does bubble size depend on pressure, and why?*

Bubble size initially increases with pressure, reaches a maximum at a critical pressure (10-20 atm) that is independent of coal rank, and then decreases as pressure increases further. The initial increase is due to increased gas generation by inhibiting evaporation of primary tars and degrading them to gas. However, bubble size for constant gas mass decreases with pressure, so ultimately the compression of the bubbles dominates the incremental gas volume generation.

2. *What two chemical agents are commonly used to increase liquid yields from coal and Type II kerogen? Why are such conditions less important for Type I kerogen?*

H₂ and hydrogen donor solvents. Type I kerogens contain more hydrogen in their structure, so additional hydrogen has a smaller percentage increase in yield, and it is unlikely that the extra expense of such a reactor is worthwhile.

3. *Volatile hydrocarbon yields during pyrolysis correlate with kerogen aromaticity.*a. *Does this mean that the pyrolysates are only aliphatic?*

No

b. *What kind of chemical structures are likely to aromatize during pyrolysis?*

Hydroaromatic, i.e., structures that are partially aromatic and partially naphthenic

c. *Do you think the kind of chemical structures from 3b would be useful during coal liquefaction? Why or why not?*

Yes, they serve as a source of reactive hydrogen for enhanced conversion of coal to liquids.

4. *What are three effects of increasing pressure during kerogen pyrolysis in a semi-open system?*

Any three of the following are correct

- Delayed oil vaporization
- Increased coke formation
- Increased cracking of long alkyl chains
- Increased gas formation
- Lower density (higher API gravity) oil product

5. *These questions deal with oil cracking.*a. *What value would you pick for the average activation energy for oil cracking without having data for the specific oil to be modeled?*

Something between 55 and 60 kcal/mol.

Paraffinic crudes and elevated pressures would indicate E at the high end of that range.

b. *If a first-order kinetic analysis of oil cracking data gave $E=30$ kcal/mol, what would you say?*

It is most certainly wrong because the material has distributed reactivity. Furthermore, it is likely that the maximum conversion increased with temperature, so the data set did not adequately decouple conversion from temperature, thereby failing to honor the isoconversional principle.

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6. If the effective activation energy for volatilization of oil and gas during kerogen pyrolysis is given by eqn. 5.2: $E_{\text{eff}} = E_{\text{true}} + 10 \cdot (1 - T/500^\circ\text{C})^2 / (1 + F) + 0.067(P_a - 1)$

a. What is the difference between the true and effective activation energies at a pyrolysis temperature of 325 °C?

For $F=0$ and $P_a=1$, $10 \cdot (1 - 325/500)^2 = 1.23 \text{ kcal/mol}$

b. What is the change in activation energy for a pressure of 20 atmospheres?

For $F=0$ and $P_a=20$, $0.067 \cdot (20 - 1) = 1.27 \text{ kcal/mol}$

c. How much would the oil evolution curve shift from atmospheric pressure to 20 atmospheres at a heating rate of 1 °C/min?

16 °C

7. What are two molecular characteristics that affect the partition coefficient of a given oil component between the liquid and vapor phases? What is the implication of that partitioning on the composition of the expelled oil?

Molecular weight and polarity

One would expect preferential expulsion of lighter, more saturated hydrocarbons.

8. What is the primary reason for an increase in API gravity for oil produced from a semi-open reactor?

Cracking to lighter hydrocarbons

9. In Figure 5.23 why does the maximum in ΔTR (ΔS2) occur at a lower maturity than the maximum in S1/TOC ?

ΔTR (ΔS2) relates to the conversion of kerogen to all products, while S1 relates to the formation of volatile oil, which often or even usually requires multiple reactions. In addition, the decrease of TOC during kerogen conversion further shifts S1/TOC to higher maturity.

10. In Figure 5.26, why does the yield of oil decrease as particle size increases? Suggest a relationship between particle size and heating rate that might lead to a constant oil yield as both are changed in concert?

The beneficial effect of H_2 on oil yield depends on it diffusing to the location where the oil is born, hence increased particle size makes it harder for H_2 to reach the critical reaction location. As the heating rate increases, particle diameter must be decreased. Figure 5.26 suggests that the particle size dependence is stronger over the ranges shown, so a doubling of the particle size might require the heating rate to be lowered by a factor of four or more.

Chapter 6 Exercises

1. *What optical property of vitrinite governs the amount of reflected light and why is it related the maturity? How is that relationship related to Vitrimat?*

The primary optical property determining reflectance is the refractive index, which can be thought of simply as a measure of how strongly the oscillating electric field in the light interacts with the electrons in the material. That interaction becomes stronger as the material becomes more aromatic.

Aromaticity is inversely related to the H/C ratio and oxygen content, which are calculated by Vitrimat. Reflectance is then calculated from correlations of elemental composition with reflectance.

More generally, reflectivity depends on the real and imaginary portions of the refractive index as described by the Fresnel-Beer equation. The imaginary portion is also known as the absorptive index, and real and imaginary indices are related through the Kramers-Kronig relationship. As the aromatic rings get larger, the absorption shifts towards the visible region, which also results in an increase in the refractive index due to off-resonance interaction. The ultimate limit of oriented aromatic sheets is graphite, which is visibly shiny.

2. *During kerogen maturation, what molar ratio of CO₂ and H₂O must be eliminated to maintain a constant H/C ratio? Which kerogen type comes closest to maintaining a constant H/C ratio during early maturation?*

H and C must be eliminated in the same ratio as they exist in kerogen, so $H_2O/CO_2 = 0.5 * (H/C)_{ker}$. For coal, with $H/C \sim 1.0$, two molecules of CO₂ are eliminated for each water molecule.

Type III kerogen, or coal, comes the closest to maintaining a constant H/C ratio during early maturation, because it has the largest amount of oxygen and therefore eliminates the most amount of mass before generating significant hydrocarbons.

3. *What are three possible reasons for vitrinite reflectance suppression, and how are they related to the chemical kinetics governing maturation and reflectance?*

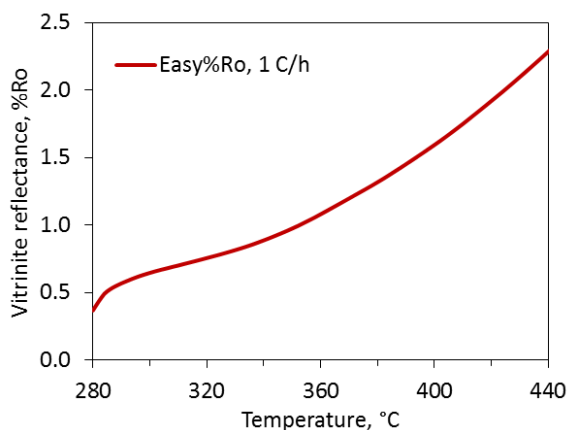
Choose three of the following four:

- A different type of source material identified as vitrinite
- A different chemical structure of the same woody source material caused by different deposition and diagenesis conditions in shales.
- Impregnation of vitrinite by bitumen
- Inhibition of vitrinite reflectance by pore pressure generated in source rocks

Chemical kinetics can influence vitrinite reflectance either directly or indirectly. If the starting material is different or if early diagenesis results in a different chemical structure, the subsequent chemical kinetics and elemental composition as a function of thermal severity will be different. Indirect effect involve the generation of pore pressure and bitumen from oil-prone macerals, which in turn affect vitrinite composition and structure. Simple swelling of vitrinite by bitumen has been demonstrated not to be important, and pressure effects, though present, are too small to account for the observed effects. The first two reasons are more likely culprits.

Global Chemical Kinetics of Fossil Fuels: How to Model Maturation and Pyrolysis

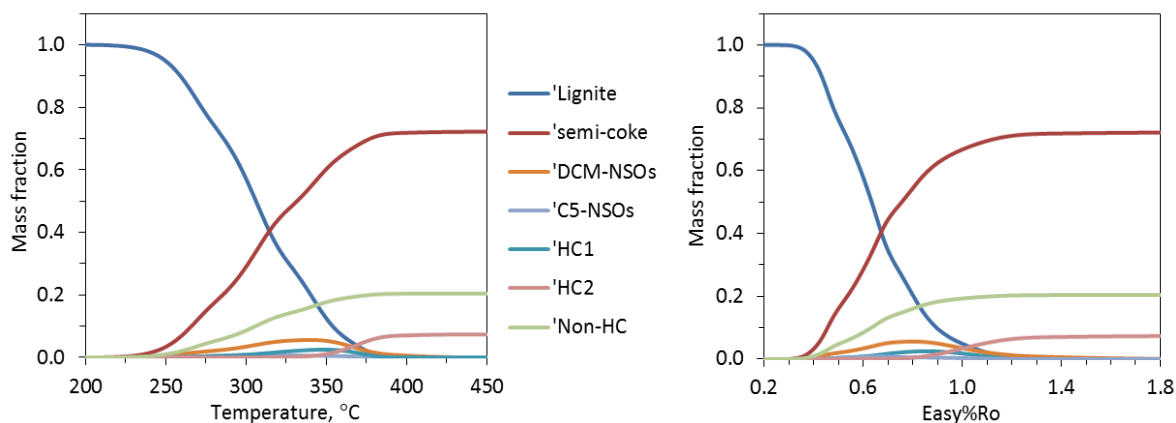
4. Construct a spreadsheet or program to calculate vitrinite reflectance using the Easy%Ro algorithm at a constant heating rate. Plot reflectance versus temperature for a heating rate of 1 °C/h.



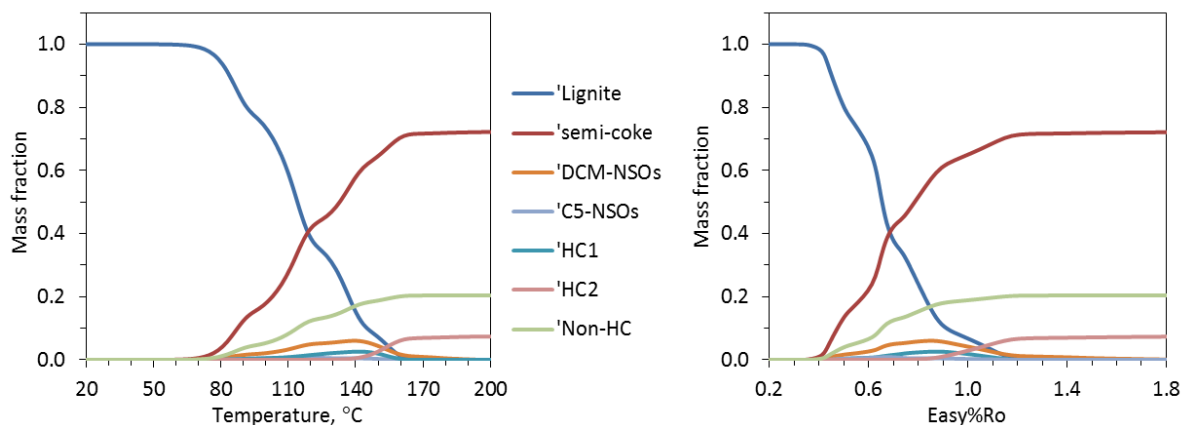
5. Construct a spreadsheet or program to calculate the compositional evolution of lignite and products in a closed system using the kinetic parameters in Tables 6.3 and 6.4.

The following calculations were made with PMOD2 and plotted in Excel.

- a. Plot the mass of each species as a function of temperature and vitrinite reflectance for a sample heated at 1 °C/h.



- b. Plot the mass of each species as a function of temperature and vitrinite reflectance for a sample heated at 3 °C/Myr.



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6. Compare the results in Figures 5.24, 6.21, and 6.22. What similarities and differences do you see between semi-open pyrolysis and hydrous pyrolysis?

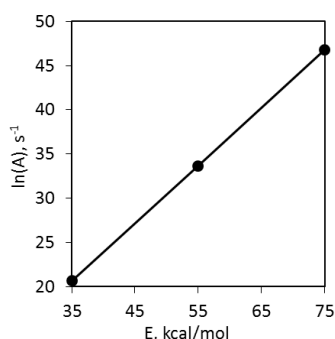
The fractionation ratios between oil and bitumen are very similar for all experiments, with asphaltenes always preferentially retained in the bitumen and saturates being partitioned roughly equally between oil and bitumen at 330 °C. The temperature dependence for semi-open pyrolysis is within the range of the three hydrous pyrolysis experiments. Hydrous pyrolysis seems to have a more preferential expulsion of saturates over aromatics compared to semi-open pyrolysis, which has more dependence on molecular weight than saturate-aromatic character.

7. Consider three reactions having the following A-E pairs: $1 \times 10^9 \text{ s}^{-1}$, 35 kcal/mol; $4 \times 10^{14} \text{ s}^{-1}$, 55 kcal/mol; $2 \times 10^{20} \text{ s}^{-1}$, 75 kcal/mol.

a. Calculate Rock-Eval T_{\max} for the three reaction pairs. What kerogen types might they represent?

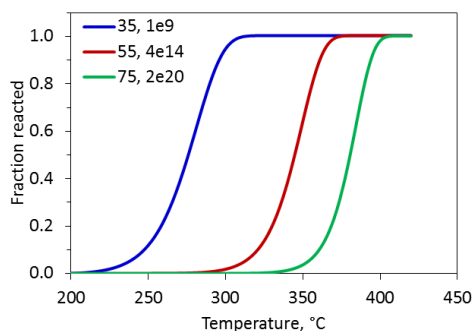
396 °C, Type II-S; 428 °C, Type II; and 440 °C, Type I

b. Construct a compensation relation plot for these three A-E pairs. What does it tell you?



The A and E values are highly correlated, and the positive slope of the line is mostly unrelated to reactivity differences, which are reflected more by a negative slope.

c. Plot the fraction reacted as a function of temperature for a heating rate of 1 °C/h. Compare the temperatures for 90% conversion to those in Figure 6.33 for the three kerogen types.



There is a large difference in the temperature for 90% conversion at 1 °C/h, ranging from about 290 to 390 °C, but all organic matter types become 90-100% reacted at 360 °C in hydrous pyrolysis.

d. What values of A are needed to have all three reactions be 90% complete at 360 °C?

Type II-S: $3.2 \times 10^9 \text{ s}^{-1}$; Type II: $4 \times 10^{14} \text{ s}^{-1}$; Type I: $4 \times 10^{21} \text{ s}^{-1}$

e. Calculate the Rock-Eval T_{\max} values for the modified A values and compare to those from 7a. What does that tell you?

Type II-S: 367 °C; Type II: 428 °C; Type I: 399 °C

It is impossible with 35 and 75 kcal/mol activation energies to pick a frequency factor that matches data over a very wide range of conditions.

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8. *What does Figure 6.42 tell us about the relationships among open-system pyrolysis, hydrous pyrolysis, and natural maturation?*

The evolution of kerogen in hydrous pyrolysis is closer to natural maturation as reflected in the open-system product distribution of the remaining kerogen as a function of its maturity.

9. *A parallel reaction model says that the reactivity of the residual material, as reflected in T_{max} for example, is simply due to preferential elimination of the lower activation energy material. Describe another mechanism that can lead to lower reactivity in the residual material.*

Retrograde polymerization reactions between aromatic rings can form very stable bonds that would be reflected in higher activation energies than for the starting material.

10. *Compare the results in Figure 6.45 for coal hydrogenation and extraction with those calculated in problem 5.*

Both show a progression of heavy to lighter products and occur over similar vitrinite reflectance ranges. However, if we assume that DCM-NSOs are comparable to asphaltenes and HC1 is similar to oil, the peak asphaltene yield is at ~0.2% higher vitrinite reflectance in Figure 6.45 and the oil is generated at ~0.1% higher reflectance in Figure 6.45. It is hard to draw any general conclusions because of the numerous differences between the two studies.

Chapter 7 Exercises

1. *You measure pyrolysis kinetics at ~450 °C and derive $A=4 \times 10^{14} \text{ s}^{-1}$ and $E=54 \text{ kcal/mol}$. One person applies them at 1500 °C and another applies them at 150 °C. Which person is making the larger extrapolation in time, and why?*

First calculate the rate constants at the three temperatures and normalize them to the 450 °C value. Although the temperature extrapolation is greater to 1500 °C, the extrapolation in time is greater to 150 °C. Application to 1500 °C decreases the time scale by 4×10^9 times, while application to 150 °C increases the time scale by a factor of 4×10^{11} times.

2. *Petroleum system modeling requires paleothermal histories.*

a. What is “backstripping”, and why is it important for calculating paleothermal histories?

Backstripping is the process of mathematically removing sediments in a stepwise manner from last to first deposited and then expanding the underlying sediments at each step to the porosity they would have had at that earlier time and depth. This is needed to calculate the thermal history of each stratum, because the temperature at each point depends on the thickness and thermal conductivity (via porosity) of the overlying and underlying strata at each time.

b. Describe two aspects of heat flow that are not captured by assuming a constant paleothermal gradient.

Here are three possible answers:

- (1) Sediment deposition or erosion can happen faster than heat flow can reach steady state, thereby causing additional time dependence to the thermal profile history in the form of a transient thermal state.
- (2) Changes in the crustal thickness (e.g., thinning or thickening by plate tectonics or thickening by rapid sediment deposition) change the distance over which the temperature difference between the asthenosphere-lithosphere boundary and surface must be spread as a function of time.
- (3) Changes in thermal conductivity of rocks as a function of lithology and porosity versus depth cause variations, sometimes very significant, in the steady-state thermal gradient versus depth.

3. *Describe the conceptual difference between the organofacies classification and the IFP Type classification system. Do you think they would lead to a significant difference in a drilling decision? Why or why not?*

The organic facies classification considers both the type of organic matter being deposited as well as the conditions under which it is deposited, particular oxygen and sulfur fugacity. The original IFP Type classification is a simpler concept based primarily on HI, which in turn, correlates with other generative properties. However, the three standard IFP kerogen types, even when allowing mixtures, do not fully cover the diversity of kerogen structure and reactivity. For example, Type II-S and I-S were introduced to account for the enhanced reactivity of sulfur sigma bonds for high-sulfur kerogens. Picking chemical kinetic parameters strictly on the basis of HI could easily cause an error of 10-20 °C in the predicted oil and gas generation temperature. Depending on the basin evolution history, this could mean as much as a km error in the predicted depth of oil and gas generation. This

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in turn could lead to a major error in the estimated volume of oil and gas likely generated in petroleum system and even the relative timing of generation and trap formation. Drilling decisions are made on a variety of factors, and this could affect the decision for a marginal case.

4. *If decompaction is defined as expansion of the mineral matrix in a rock, how would it be possible for porosity to increase if decompaction were not allowed?*

Porosity can increase by removing some of the solid components of the rock. Two examples are dissolution of inorganic components and conversion of kerogen to oil and gas.

5. *The transformation ratio is related to the hydrogen index by $TR = (1 - HI/HI_0)/(1 - HI/1200)$.*

- a. *Why is the 1200 factor there?*

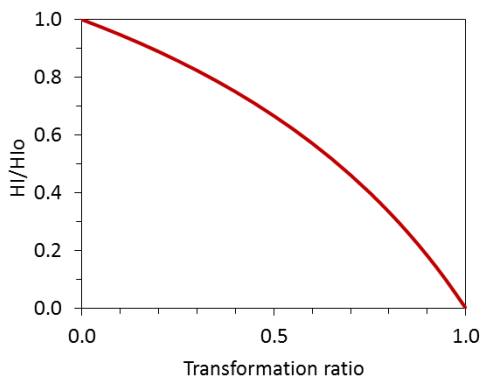
It is approximately the mass of hydrocarbons generated per unit carbon (mg/g). It is consistent with a kerogen carbon content of 83%.

- b. *Derive a formula for TR involving S₂ and TOC assuming that half the kerogen is converted to oil and gas during maturation.*

The assumption that half the kerogen is converted to oil and gas is equivalent to assuming $HI_0 = 600$ mg/g within the approximation of the starting equation, so such an equation is simply

$$TR = (1 - S_2/TOC/600)/(1 - S_2/TOC/1200).$$

- c. *Calculate and plot TR as a function HI/HI_0 for the same assumption. What is its shape, and what are the implications if you want to estimate the fraction of oil and gas generated from HI?*



The relationship is nonlinear, even though people assume it is linear. Assuming you know HI_0 , you must use the equation above to estimate TR. Even so, reality is more complicated, because natural maturation and Rock-Eval give different yields of oil and gas.

6. *How does an increase in the solubility oil in kerogen affect the ratio of expelled oil and gas in the Pepper-Corvi model, and why?*

The Pepper-Corvi model is based on the assumption that the principal factor effecting the timing of oil and gas expulsion from the source rock is when the kerogen becomes saturated with oil and gas. If the oil is retained in the kerogen for a longer time, it has a longer time to continue decomposing to oil and gas, and the expelled fluids will reflect that additional secondary cracking.

7. *What is the difference between true and modified in-situ processes, and what physical property of oil shale motivates different solutions to the resulting processing constraint?*

The difference is the introduction of porosity into the oil shale by some type of rubbleization for modified in-situ retorting. The permeability of oil shale is very low ($<1\mu d$), so the porosity is needed

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if heat is to be transferred throughout the formation via gas flow. True in-situ retorting relies primarily on thermal conduction over longer times.

8. Consider conductive heating methods for a true in-situ oil shale process.

a. What two factors are traded off when considering well spacing?

The time to completely heat the formation between the wells increases with well spacing. Placing the wells closer together shortens the time for complete recovery but increases costs by needing to drill more wells.

b. Why would one use horizontal wells rather than vertical wells when the resource is significantly thinner than the overburden.

Drilling costs increase with distance drilled. Proper spacing of heaters requires directional drilling in either case, so horizontal drilling decreases overall cost by increasing the ratio length of heated well to parasitic well through the overburden.

c. What are the advantages of using planar heat sources rather than linear heating sources?

The time to heat the formation depends on, among other factors, the surface to volume ratio of heater to shale. Planar heat sources have much more surface area per well than linear heating sources.

9. You are designing a plug-flow surface reactor using Type I oil shale. The rock has a yield of 30 gal/ton, and you want to produce 5,000 bbls/day.

a. What value of A and E would you choose in the absence of direct measurement?

$A = 4.5 \times 10^{13} \text{ s}^{-1}$; $E = 53 \text{ kcal/mol}$

b. If the process operates at 480 °C and you design for 97% conversion, what is the best estimate for the reactor volume?

First calculate the time required for retorting: $k = 0.0187 \text{ s}^{-1}$; $\text{conversion} = e^{-kt}$; $t = 187 \text{ s}$, or 3.12 min, to achieve 97% conversion.

$30 \text{ gal/ton} \times 0.97 = 29.1 \text{ gal/ton}$, so $(5000 \text{ bbls/day}) \times (42 \text{ gal/bbl}) \times (1 \text{ ton}/29.1 \text{ gal}) = 7216.5 \text{ tons/day}$.

Assuming an oil shale density of 2.2 g/cm^3 ,

$\text{Rock volume} = (7216.5 \text{ tons/day}) \times (907 \text{ kg/ton}) / (2200 \text{ kg/m}^3) = 2975 \text{ m}^3/\text{day}$

One must also assume a void volume in the reactor. Packed beds are typically about 50% intergranular porosity, so $(2975 \text{ m}^3 \text{ rock/day}) \times (2 \text{ m}^3 \text{ reactor/m}^3 \text{ rock}) \times (1 \text{ day}/1440 \text{ min}) \times 3.12 \text{ min} = 12.9 \text{ m}^3$. Some contingency should be added for good measure.

10. Produced oil and gas compositions can be used to diagnose retorting conditions and reasons for loss of oil yield.

a. What two pyrolysis conditions affect alkene/alkane ratios?

Temperature and inert gas diluent

b. If a process exposes a portion of the oil to very high temperatures outside the shale particles, what two ranges of alkene/alkane ratios can be used to determine coking and cracking/combustion losses separately?

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All alkene/alkane ratios start with the imprint of intraparticle coking due to slower heating inside the particle. If a small portion of that oil sees very high temperatures, it will be cracked mostly to $<C_{10}$, so the $>C_{10}$ components from oil that does not see the high cracking temperatures will retain the coking information. In contrast, the high temperature cracking will produce much light hydrocarbon gas, so increased C_2 and C_3 alkene ratios will be diagnostic of that degradation. (Combustion involves very high temperatures, for which naphthalene is a good diagnostic.)

11. What is the difference between direct and indirect coal liquefaction? Name two indirect processes that lead to liquid hydrocarbon fuels.

Direct liquefaction converts the molecular structures in the coal to liquids with modest changes, while indirect liquefaction gasifies the coal to H_2 and CO (syngas) and then reconstructs liquids from scratch. Examples:

- (1) Fischer-Tropsch, which uses an iron or cobalt catalyst to grow alkane chains directly
- (2) Conversion of syngas to methanol, followed by conversion of methanol to gasoline using a zeolite catalyst

12. Continuous-flow, stirred-tank reactors are useful when two process streams interact.

a. What conversion is achieved in a single continuous flow, perfectly stirred reactor compared to a single plug flow reactor of the same total volume that achieves 95% conversion?

First solve eqn. 7.2 to find kt for 95% conversion (5% unconverted): $kt = -\ln(0.05) = 3.00$

Next use eqn. 7.3, fraction unconverted $= 1/(1+3.00) = 0.25$, so conversion is 75%

b. The Shenhua direct liquefaction process has two stirred reactors in series (Fig. 7.20). If the same stirred-tank reactor volume is split into two sequential reactors, what conversion occurs?

If the volume of each reactor is halved, kt is halved in each, but the fraction unconverted is squared for two reactors.

$$C_{out}/C_{in} = (1/(1+1.50))^2 = 0.16, \text{ so conversion is } 84\%$$

13. What are the three stages for burning a coal particle?

Drying, combustion of volatiles outside the pyrolyzing coal particle, and combustion of char

14. You measure rate constants for burning coal particles of 1 s^{-1} at $550\text{ }^\circ\text{C}$ and 1000 s^{-1} at $1500\text{ }^\circ\text{C}$.

a. What are the effective first-order A and E values?

If $k = Ae^{-E/RT}$, $\ln(k) = \ln A - E/RT$; $-E/R = \ln(1/1000)/(1/(550 \cdot 273) - 1/(1500 \cdot 273)) = -10610$; $E = 21.1\text{ kcal/mol}$

b. How does that E compare with accepted values for pyrolysis of raw coal and for combustion of char?

Pyrolysis is typically 50-55 kcal/mol. Char oxidation is more complicated, involving diffusion and adsorption-desorption phenomena, so activation energies range from 20-40 kcal/mol, with the higher values more likely indicative of pure chemical reaction control.

c. Explain the source of the difference.

The overall apparent E is far lower than the best one for pyrolysis and on the low end of the combustion values, so it probably is greatly affected by heat and mass transfer resistance.