TWO-STAGE OXIDATION REACTION IN A POROUS MEDIUM

L. FURTADO, D. MARCHESIN, AND J. BRUINING

This report contains four sections. The first section discusses the theory behind the two-phase oxidation problem. Each of the other three sections discusses a specific variation in the parameters of the system. Namely, the second section of this report discusses the effect of varying the heat transfer coefficient, k. The third section involves varying the activation energy of the alcohol, E_F. In the fourth section, the heat transfer coefficient was again modified, albeit with more specific conditions in mind. The system of ODEs was solved numerically using MATLAB®, and specifically the numerical ODE solver ode45.

1. THEORY

We consider a vessel filled with sand and olefin at an initial concentration B_0 [mole/m3-porous medium] of, say, 893 moles/m3. Oxygen is present at a constant saturation. We consider a low temperature oxidation (LTO) and a high temperature oxidation (HTO) reaction. The LTO reaction (1.1) converts the olefin to alcohol, i.e.,

$$C_nH_{2n} + \frac{n}{2}O_2 \rightarrow C_nH_n(OH)_n, \tag{1.1}$$

and a high temperature oxidation reaction (1.2)

$$C_nH_n(OH)_n + nO_2 \rightarrow nCO_2 + nH_2O. \tag{1.2}$$

The initial alcohol concentration $F_0 = 0$. The initial temperature is T_0, which is equal to the outside temperature.

Using the rule of thumb that the reaction heat per mole of oxygen $\Delta H_{O_2} = 450$ kJ/mole is roughly the same, we observe the second reaction generates twice as much heat as the first reaction. For reasons of concise notation we use B as the molar concentration [mole/m3-porous medium] of C_nH_{2n} and F as the molar concentration of $C_nH_n(OH)_n$. The olefin oxidation rate is considered to be proportional to B, whereas the alcohol oxidation rate is proportional to F. As oxygen is abundant we included the oxygen concentration dependence in the rate coefficients k_B and k_F as a constant. The rate r_B of the olefin oxidation reaction (1.1) is

$$\frac{dB}{dt} = -r_B = -A_B exp\left(-\frac{E_B}{RT}\right)B, \tag{1.3}$$

where A_B is the frequency factor and E_B is the activation energy. The rate of the HTO reaction (1.2) is called r_F.The overall rate of the alcohol concentration combines reactions (1.1) and (1.2), i.e.,

$$\frac{dF}{dt} = r_B - r_F = A_B exp\left(-\frac{E_B}{RT}\right)B - A_F exp\left(-\frac{E_F}{RT}\right)F, \tag{1.4}$$

where A_F is again a frequency factor and E_F is an activation energy. The temperature equation expresses that the heat of reaction heats up the porous medium with heat capacity $\rho_m c_m$=2103kJ/m^3/K and reads

$$\rho_m c_m \frac{dT}{dt} = \left(\frac{1}{2} A_B exp\left(-\frac{E_B}{RT} \right) B + A_F exp\left(-\frac{E_F}{RT} \right) F \right) n\Delta H_{O_2} + \kappa (T_0 - T), \tag{1.5}$$

where $n\Delta H_{O_2}$ describes the heat of reaction of n oxygen molecules. The last term in the heat equation describes the heat transfer between the medium and the surroundings. The following table is also based on Lin et al. [2].

	Kumar [1]	Lisbon	Athabasca	Crude A	Crude B
$\mathrm{A}_F(days^{-1})$	1.73×10^12	2.332×10^17	3.369×10^18	4.153×10^13	1.346×10^5
$\mathrm{E}_F(cal/mole)$	40506.	52686	53582	40506	12069
$\mathrm{A}_B(days^{-1})$	2.1×10^9	-	6.429×10^14	5.053×10^10	2.323×10^7
$\mathrm{E}_B(cal/mole)$	35811	-	47422	35810	25025

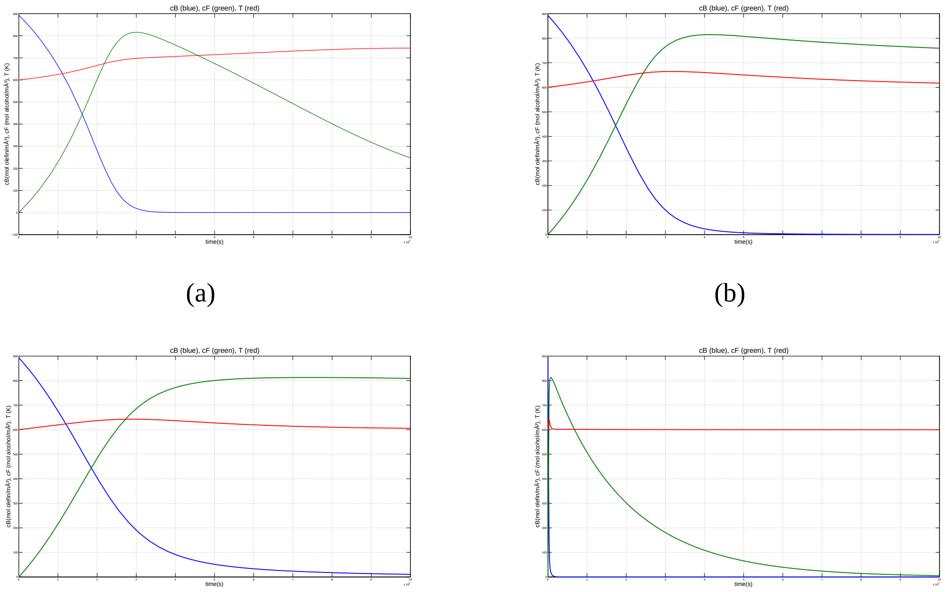
	Kumar [1]	Lisbon	Athabasca	Crude A	Crude B
$\mathrm{A}_F(sec^{-1})$	2.00×10^7	2.70×10^12	3.90×10^13	4.81×10^8	1.56
$\mathrm{E}_F(J/mole)$	1.70×10^5	2.204×10^5	2.24×10^5	1.7×10^5	50500
$\mathrm{A}_B(sec^{-1})$	24310	-	7.44×10^9	5.85×10^5	269
$\mathrm{E}_B(J/mole)$	1.5×10^5	-	1.20×10^5	1.50×10^5	1.05×10^5

2. VARYING ONLY THE HEAT TRANSFER COEFFICIENT

Initially the heat transfer coefficient, k, was varied, keeping all other parameters constant. Because the conversion from olefin to alcohol is a LTO reaction, one predicts that changing k in the system will not affect the speed of olefin oxidation. Plotting a solution to the system of ODEs (corresponding to initial conditions $T_0 = 600K, B_0 = 893, F_0 = 0$) that models this two-phase oxidation, Fig. 1, confirms that very little change in the speed of olefin oxidation is observed with changing values of k. Alcohol is oxidized in a high temperature oxidation reaction. Thus, one predicts that increasing k will result in a significantly slower alcohol oxidation. This is observed from the plots, and for a large enough k one can say that, in all practical terms, alcohol reacts so slowly that no alcohol oxidation can be observed in a reasonable experimental time; see Fig. 1.

3. VARYING ONLY THE ACTIVATION ENERGY OF THE ALCOHOL

An extremely slow alcohol oxidation may be a problem. Thus, secondly, a large k value ($k = 1$) was chosen to remain constant, and parametric curves of olefin and alcohol concentrations and temperature, as functions of time, were plotted, varying the activation energy of the alcohol (E_F) and keeping all other values constant. As was expected, a lower E_F resulted in quicker alcohol oxidation. Three distinct cases, modifying the E_F, were observed. In the first case, that with the lowest E_F, Fig. 2(a), two distinct regimes, one with insignificant temperature increase and one with reasonable temperature increase in the oxidation of olefin (and production of alcohol) can be observed. In the second case, Fig. 2(b), the first regime, the regime with no temperature increase, disappears. In both the first and second cases all the alcohol is oxidized before the temperature begins to drop. In other words, the point in time where the last amount of alcohol is oxidized is the point where the maximum temperature is observed. The third case, Fig. 2(c), is initially similar to the second, but differs from both previous cases in that the temperature falls substantially prior to all the alcohol being completely oxidized.



(a) (b)

(c) (d)

FIGURE 1. Olefin (blue) and alcohol (green) concentrations (mol/m3), and temperature in Kelvins (red) versus time. Using modified crude B, doubling alcohol frequency factor and activation energy, and initial temperature of 600K (these parameters remain the same throughout all other plots in this paper, unless otherwise indicated). 1(a): $k = 0.2$; 1(b): $k = 0.6$; 1(c): $k = 1$; 1(a): $k = 1$ plotted over a larger time scale, showing that eventually the alcohol will react completely.

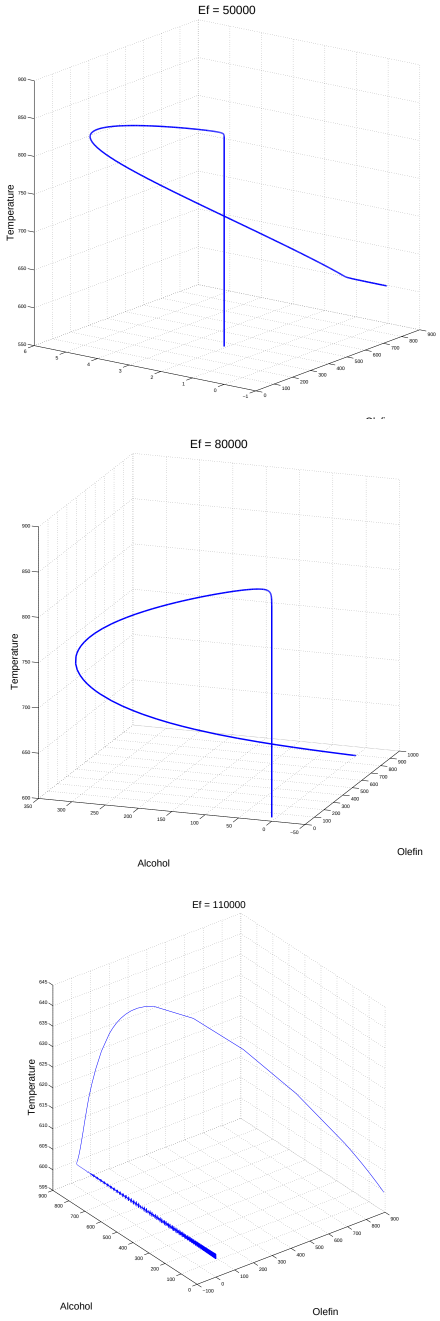
4. VARYING ONLY THE HEAT TRANSFER COEFFICIENT FOR EACH CASE IN SECTION 3

Upon observing the three cases in Section 3, deeper understanding of them was obtained by varying k values for each case, and analysing the plots obtained by parametrizing olefin and alcohol concentrations and temperature with respect to time.

4.1. **Increasing the Heat Transfer Coefficient.** Decreasing the value of k produced very little change in the orbits with $E_F = 50000$ and $E_F = 80000$, Figs. 7(a) and 7(b), respectively. Decreasing k with $E_F = 110000$ produced a visible change in the orbits, Fig. 7(c). When k is 0.1, the temperature drops relatively quickly compared to the oxidation of alcohol. The temperature decreases to the initial temperature before all the alcohol is oxidized. When k is decreased further, the temperature does not decrease prior to the alcohol being completely oxidized, and the orbits resemble those in Figs. 7(a) and 7(b).

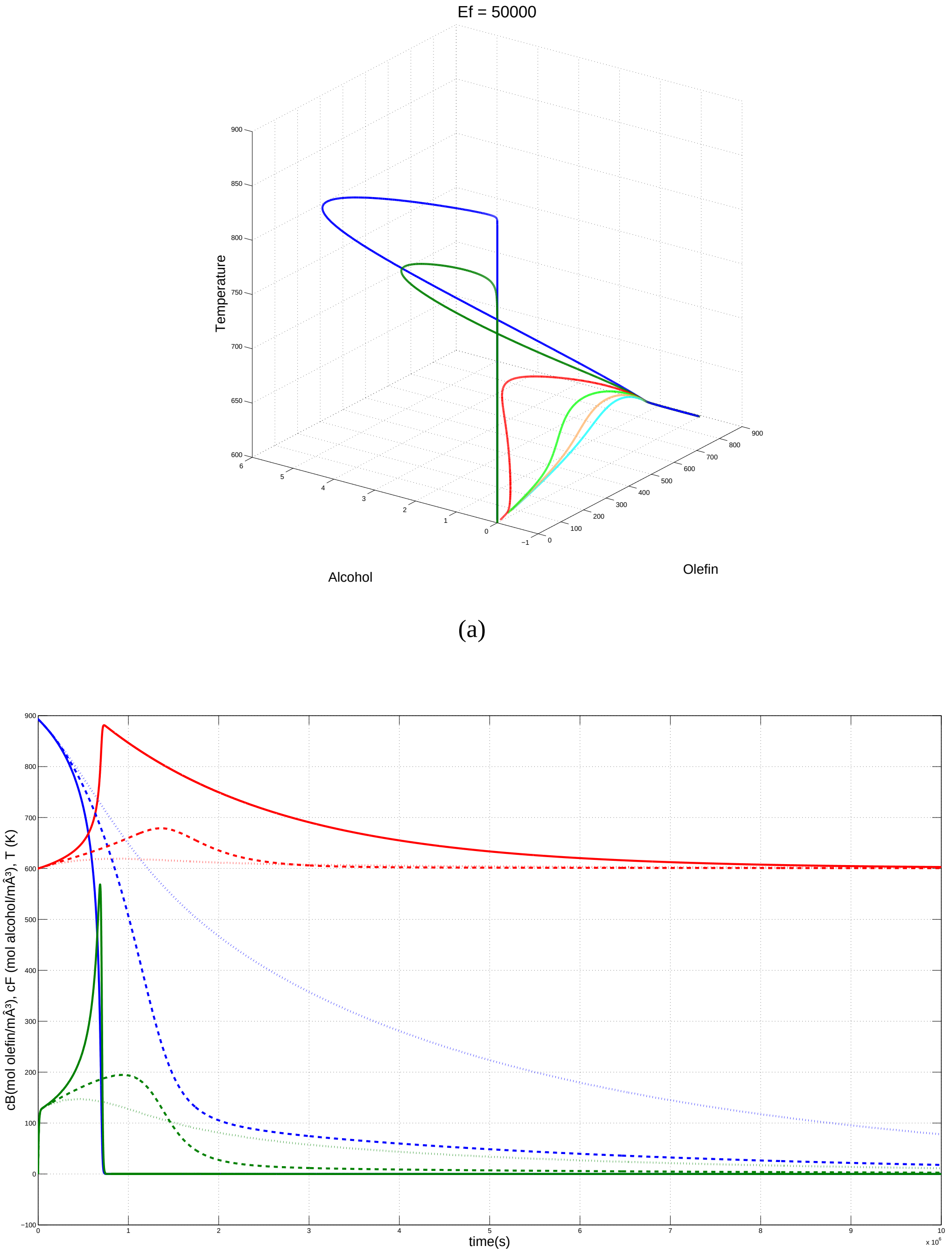
4.2. **Decreasing the Heat Transfer Coefficient.** An increase in k provokes a slower reaction of both olefin and alcohol and a smaller overall increase in temperature. The slower reaction of both olefin and alcohol provokes smaller concentrations of both species at any time during the process. Furthermore, increasing k when $E_F = 50000$ provokes no change in the first regime, Fig. 3, the regime with insignificant temperature increase. For $E_F = 80000$ and $E_F = 110000$, Fig. 4 and Fig. 5 respectively, increasing k results in a change qualitatively similar to when $E_F = 50000$. Furthermore, increasing k when $E_F = 110000$ negligibly affects the relationship between olefin concentration and alcohol concentration. This does not occur when $E_F = 80000$ and $E_F = 50000$.

In other words, plotting on the same olefin-concentration versus alcohol-concentration axes curves with increasing *k* values produces a nearly perfect overlap, Fig. 6(c).



(c)

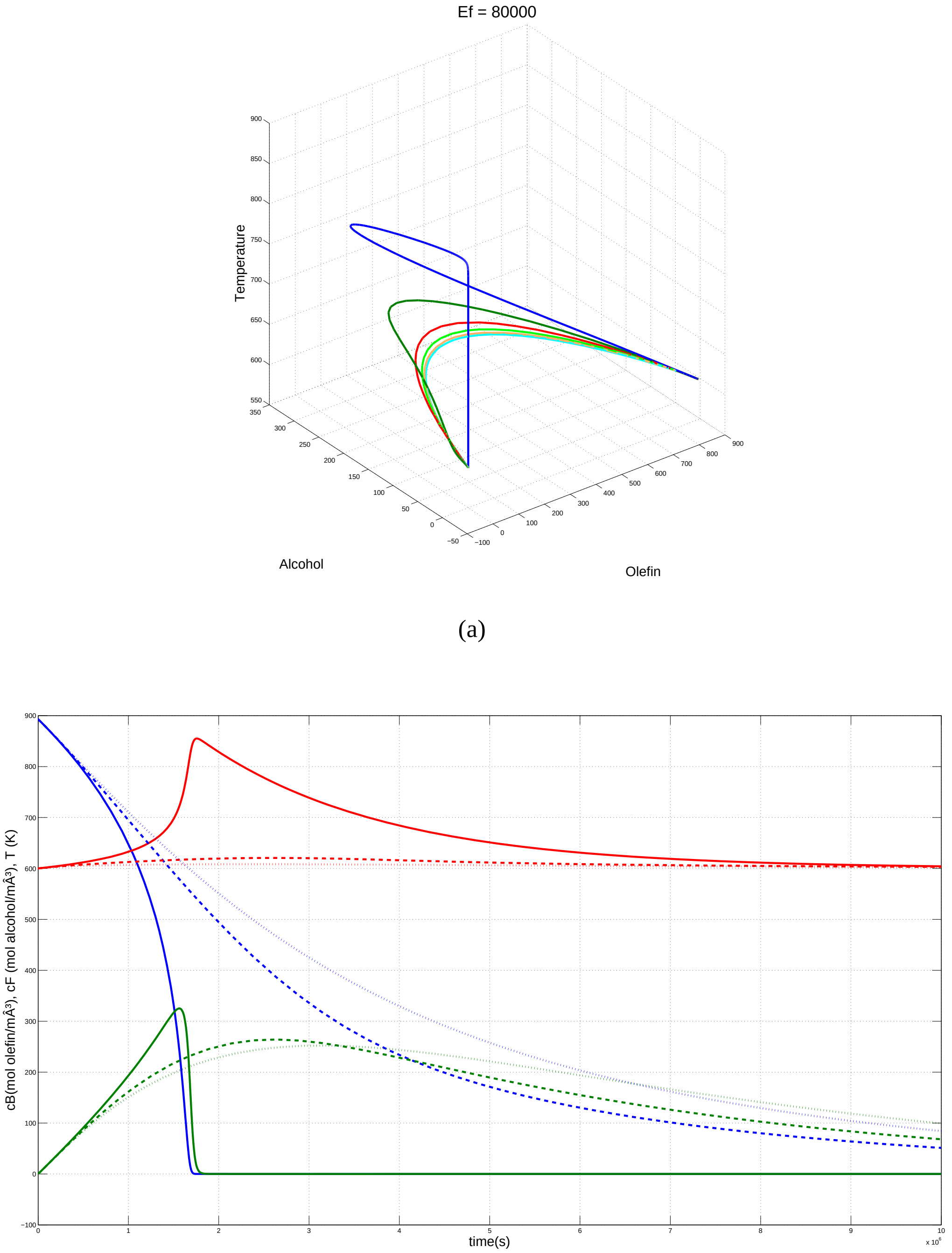
FIGURE 2. Altering activation energy of the alcohol. 2(a): $E_F = 50000$; 2(b): $E_F = 80000$; 2(c): $E_F = 110000$.



(a)

(b)

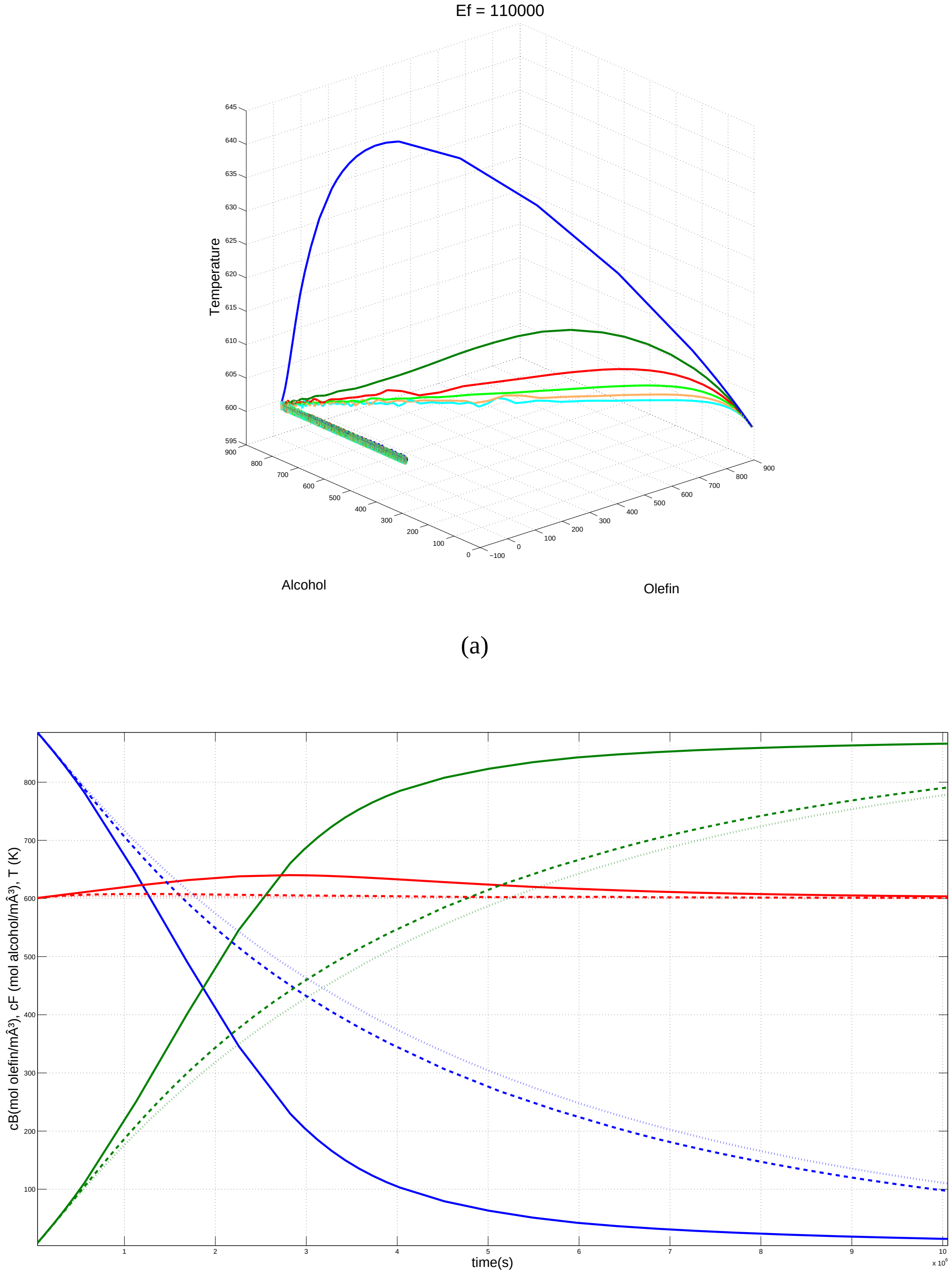
FIGURE 3. 3(a): $E_F = 50000$. k = 1 (blue), 3 (green), 5 (red), 7 (light green), 9 (orange), 11 (cyan). 3(b): Olefin concentration (blue), alcohol conentration$\times$100 (green), temperature (red), $k = 1$ (full lines), $k = 5$ (dashed lines), $k = 9$ (dotted lines).



(a)

(b)

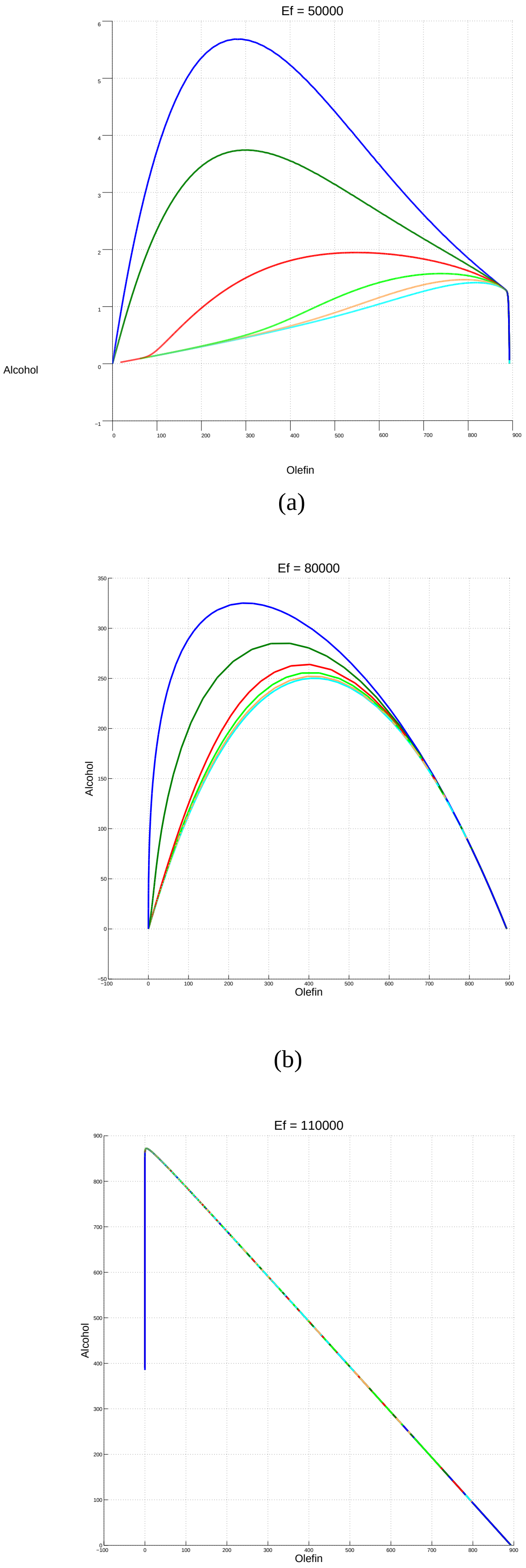
FIGURE 4. 4(a): k = 1 (blue), 3 (green), 5 (red), 7 (light green), 9 (orange), 11 (cyan). U 3(b): Olefin concentration (blue), alcohol conentration (green), temperature (red), $k = 1$ (full lines), $k = 5$ (dashed lines), $k = 9$ (dotted lines).



(a)

(b)

FIGURE 5. 5(a): $k = 1$ (blue), 3 (green), 5 (red), 7 (light green), 9 (orange), 11 (cyan). 3(b): Olefin concentration (blue), alcohol conentration (green), temperature (red), $k = 1$ (full lines), $k = 5$ (dashed lines), $k = 9$ (dotted lines).

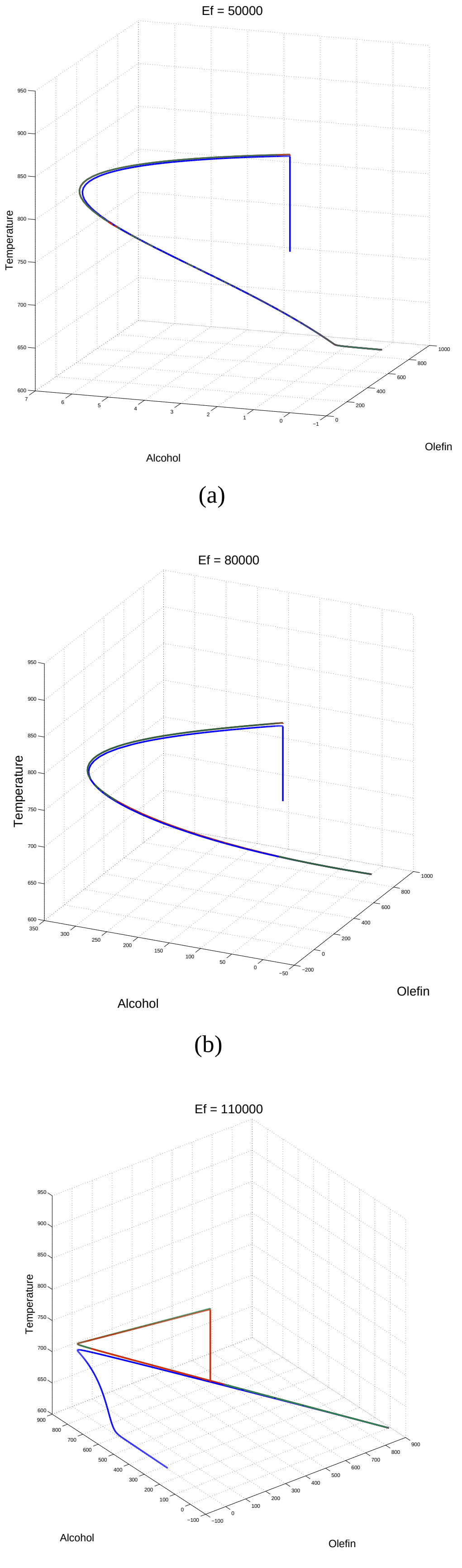


(a)

(b)

(c)

FIGURE 6. $k = 1$ (blue), 3 (green), 5 (red), 7 (light green), 9 (orange), 11 (cyan). 6(a): $E_F = 50000$; 6(b): $E_F = 80000$; 6(c): $E_F = 110000$.



(a)

(b)

(c)

FIGURE 7. k = 0.1 (blue), 0.001 (green), 1e-5 (red). Decreasing k produces very little effect on the orbits when $E_F = 50000$, 7(a), and $E_F = 80000$, 7(b). When $E_F = 110000$, 7(c), decreasing k produces significant change in the orbits.

Acknowledgements: The authors gratefully acknowledge the financial support provided by FAPERJ: Cientista do Nosso Estado under Grant E-26/102.723/2008. L. F. would like to gratefully thank F. Furtado for discussions and enlightenment concerning this project.

REFERENCES

[1] M. Kumar. Simulation of Laboratory In-Situ Combustion Data and Effect of Process Variations. paper SPE 16027, Ninth SPE Symposium on Reservoir Simulation held in San Antonio, Texas. February 1-4. 1987:1-4.

[2] C.Y. Lin, W.H. Chen, and W.E. Culham. New kinetic models for thermal cracking of crude oils in in-situ combustion processes. SPE Reservoir Engineering, 1987.

INSTITUTO DE MATEMÁTICA PURA E APLICADA, ESTRADA DONA CASTORINA 110, 22460 RIO DE JANEIRO, RJ, BRAZIL
E-mail address: `lcf2125@columbia.edu`

INSTITUTO DE MATEMÁTICA PURA E APLICADA, ESTRADA DONA CASTORINA 110, 22460 RIO DE JANEIRO, RJ, BRAZIL
E-mail address: `marchesi@impa.br`

DIETZ LABORATORY, CENTRE OF TECHNICAL GEOSCIENCE, MIJNBOUWSTRAAT 120, 2628 RX DELFT, THE NETHERLANDS
E-mail address: `J.Bruining@tudelft.nl`