CHEMICAL ENGINEERING TRANSACTIONS Volume 24, 2011
Editor Sauro Pierucci

DOI: 10.3303/CET1124071

Computational Approach for Studying the Laser Radiation Thermal Cracking Process of Heavy Petroleum Fraction: Optimization of Laser Operational Conditions

Oscar Javier Celis[1], Laura Plazas Tovar[2], Andre Luiz Jardini[1], Christiane Siegel[1], Ruben Maciel-Filho[1] , Maria Regina Wolf-Maciel[2]

[1] Laboratory of Optimization, Project and Advanced Control, School of Chemical Engineering, State University of Campinas – UNICAMP, Campinas-SP, Brazil.
[2] Laboratory of Separation Process Development, School of Chemical Engineering, State University of Campinas – UNICAMP, Campinas-SP, Brazil.

The temperature distribution related to the radiation thermal cracking process of a heavy petroleum fraction was identified by simulations using ANSYS 12.1 software. To determine the best laser parameters (laser power beam and scanning speed), a set of mathematical models (maximum and minimum temperature, time) was developed from a full 2^2 factorial design. Laser power beam and scanning speed in the range of 28-32 W and 1.8-2.2 m/s, respectively, were identified as the best set of radiation thermal cracking process parameters.

1. Introduction

Radiation-thermal cracking (RTC) processing has been developed as a new technology for the thermal cracking of heavy petroleum fractions with substantial advantages over conventional processes since it is applied directly over the petroleum fraction surface transforming heavy molecules of hydrocarbons into lighter molecules. Laser surface treatment presents substantial advantages over conventional processes e.g. low operational cost, attains higher temperatures in short times, easy local control with high precision of the laser operational parameters on the surface. Nowadays, the most laser technique used is on the manufacturing industry especially in the laser forming process by laser-induced non-uniform thermal stress (Yongjun et al, 2007). Because of high temperature gradients can be generated in the irradiation area, in the case of thermal cracking of petroleum fractions, temperature gradients must be established, otherwise undesired reactions will take place. For this reason, the main objective in this study is to identify the heat thermal transfer into petroleum phase to control the cracking temperature distribution, therefore better values of laser operational conditions as well as laser beam power and scanning speeds were found.

2. Heat transfer analysis

The transient temperature field generated during the laser cracking process is based on the mechanism of heat conduction. The governing equation of the heat conduction can be expressed as follows:

Please cite this article as: Celis O.J., Plazas Tovar L., Jardini Munhoz A.L., Siegel C., Maciel Filho R. and Wolf Maciel M.R., 2011, Computational approach for studying the laser radiation thermal cracking process of heavy petroleum fraction: optimization of laser operational conditions, Chemical Engineering Transactions, 24, 421-426
DOI: 10.3303/CET1124071

$$\rho \cdot C_P \cdot \left(\frac{\partial T}{\partial t} + \vec{\upsilon} \cdot \nabla T \right) + \nabla \vec{q} = H_{gen} \qquad (1)$$

where ρ is the material density (kg/m^3), Cp is the specific heat (J/kg.K), v is the velocity vector in (m/s), T is the temperature (K), q is the heat flux vector , H_{gen} is the internal heat generation (W/m^3) and ∇T is the temperature gradient operator. The heat flux vector can be written in terms of thermal gradients as:

$$\vec{q} = -[K] \cdot \nabla T, [K] = \begin{bmatrix} K_{xx} & 0 & 0 \\ 0 & K_{yy} & 0 \\ 0 & 0 & K_{zz} \end{bmatrix} \qquad (2)$$

where $[K]$ is the conductivity matrix, K_{xx}, K_{yy} and K_{zz} are thermal conductivity in the element x, y and z directions, respectively.

We assumed uniform thermal conductivity K (W/m.K), heat conduction within the specimen and free convection between the surfaces of the specimen and the surrounding air, but thermal radiation is neglected, the heating phenomena due to phase changes are neglected and the scanning speed is dependent of the dwell time and not as a function dependent of either x, y and z plane.

Internal heat generation term is arising from laser system and from endothermic enthalpy of the reactions. However, the second term is negligible in comparison with the first, thus:

$$H_{gen} = \frac{P}{V} - \Delta H_s = \frac{P}{\pi \cdot \omega^2 \cdot \delta} \qquad (3)$$

where P is the laser beam power (W), V is the irradiated volume (m^3), ΔH_S is the enthalpy of cracking reactions, ω is the laser beam radius (m) and δ is the absorption depth (m). The interaction time between the laser and certain point of volume is called dwell time yield (Scarparo et al, 1997):

$$t_d = \frac{2\omega}{V_s} \qquad (4)$$

where V_s is the scanning speed (m/s). Combining Eqs. (1-3) yields:

$$\rho \cdot C_P \cdot \left(\frac{\partial T}{\partial t} \right) = \frac{\partial}{\partial x}\left(K_{xx} \cdot \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y}\left(K_{yy} \cdot \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z}\left(K_{zz} \cdot \frac{\partial T}{\partial z} \right) + \frac{P}{\pi \cdot \omega^2 \cdot \delta} \qquad (5)$$

3. Finite volume modeling

The Fig. 1 shows a schematic view of laser cracking of a heavy petroleum fraction volume. The heat transfer analysis is defined in one point of irradiation on the material surface, where the irradiation time or dwell time is dependent of the scanning speed. The model is represented by two concentric cylinders in which the center cylinder is the irradiated volume. A laser-scanned geometry of a square of 12x12 cm was programmed, furthermore in the control volume (cylinder) the term of internal heat generation is zero (H_{gen}=0) during the scanning path time until the next dwell time. An atmospheric petroleum residue (R) derived from a heavy petroleum was irradiated. The material properties for heavy petroleum fraction used in the simulation are given in the Table 1.

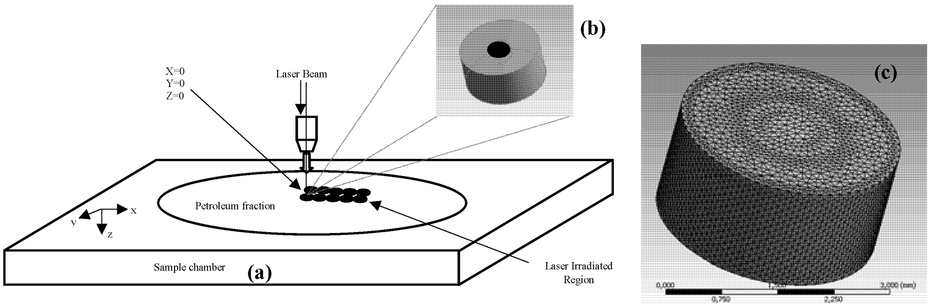


Figure 1: A schematic view of laser thermal cracking (a), control volume (b) and CFX-mesh (c) of petroleum fraction

Table 1: Material properties of atmospheric petroleum residue R

Property	Value/Function	Operating range	Source/Method
Density (kg/m^3)	963.4	298.15 K	ASTM designation D70
Specific Heat(J/kg.K)	$C_P = -2.70028 + 3.58301\exp\left(\frac{T}{1194.96017}\right)$	300-600K	Continuous thermodynamic approach (Celis, 2010)
Thermal Conductivity (W/m.K)	$K = 0.04997 + 0.79976\exp\left(\frac{-T}{138.21065}\right)$	300-600K	Continuous thermodynamic approach (Celis, 2010)
Absorption depth (m)	4.59x10^{-4}	-	Beer-Lambert law/Infrared method
Thermal cracking (K)	745.90	-	Differential scanning calorimetry (DSC)

The numerical model was solved using the commercial finite volume analysis code ANSYS 12.1. In this case to solve the temperature gradients a volume mesh was programmed, CFX-mesh method was used in which 96693 tetrahedral volumes and 18165 nodes were designed.

The boundary conditions pertinent to the heating process assumed at the free surface (in *x-y* plane at *z=0*) are those of convection to stagnant air. At that point, a heat transfer coefficient value of 5x10^{-6} W/mm^2.K was chosen. In relation to the other surfaces, the boundary conditions were properly assumed by the software as it was informed that conductive heat transfer was considered.

At x and $y = \infty \rightarrow T = T_\infty \left(T_\infty = 295.15K\right)$ (6)

Initially the petroleum sample is assumed to be at a room temperature (T_∞); therefore, the initial condition becomes: at $t = 0 \rightarrow T = T_\infty$ (7)

4. Statistical factorial design

Laser cracking operating conditions were planned based on statistical factorial design. The statistical software STATISTICA 7 from Statsoft Inc was used to create the design matrix and analyze the simulation data. Laser power beam (P) and scanning speed (V_s) were considered as input factors. Each factor and its studied range were fitted based on previous factorial design in order to define better conditions related to the cracking temperature distribution. Input factors, level setting values and the responses are presented in Table 2.

Table 2: Design matrix with independent process variables and simulation responses.

Std order	Actual levels: (Coded form/Real value)		Response values		
	Laser power beam, P(W)	Scanning speed, V_s (m/s)	T_{min}(K)	T_{max} (K)	*Time* (s)
1	-1 (28)	-1 (1.8)	391.22	761.64	3.4072
2	1(32)	-1(1.8)	404.18	835.93	3.4072
3	-1(28)	1(2.2)	385.13	733.33	2.7890
4	1(32)	1(2.2)	390.67	801.45	2.7890
5	0(30)	0(2.0)	393.45	783.76	3.0672

Full 2^2 factorial design was used as a statistical design of experiment (DOE) technique to develop mathematical models relating the laser cracking parameters to each of three responses of the radiation thermal cracking: minimum temperature (defined in a point at 40% of ratio from center volume control), maximum temperature (at thermal cracking temperature) and time reached at T_{max}. The adequacies of the models developed and their significant linear and interaction model terms were measured by analyzing variance in a confidence interval of 90%.

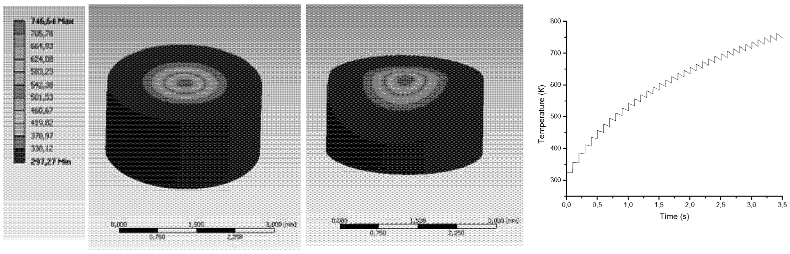
5. Results and Discussion

Figure 2 shows the temperature distribution where the cracking temperature was reached. Statistical analysis results reported that the best range of parameters laser are 28-32 W and 1.8-2.2 m/s for laser power beam and scanning speed, respectively. Moreover, for the minimum temperature model (T_{min}), the ANOVA table shows (Table 3) that the linear term of laser power (P), scanning speed (V_s), and two-factor interaction of laser power by scanning speed (P-V_s) are significant model terms. However, this same interaction showed no significance for the maximum temperature (T_{max}) model. In the case of *time* model, only the linear term of scanning speed is significant model term. Effects of these individual significant model terms and their interactions on T_{min}, T_{max} and *time* have also been illustrated graphically in Figure 3. From the results summarized in Table 4, it is, therefore, apparent that the developed models are fairly accurate and can be used for further analyses. The final mathematical models in terms of coded factors as derived by design statistic software with a confidential interval of 90% are presented below:

Minimum temperature, $T_{\min} = 392.9318 + 4.6628 \cdot P - 4.9002 \cdot V_S - 1.8547 \cdot P \cdot V_S$ (8)

Maximum temperature, $T_{\max} = 783.2220 + 35.6025 \cdot P - 15.6975 \cdot V_S$ (9)

Time reached, $Time = 3.091920 - 0.3091 \cdot V_S$ (10)



(a) (b) (c)

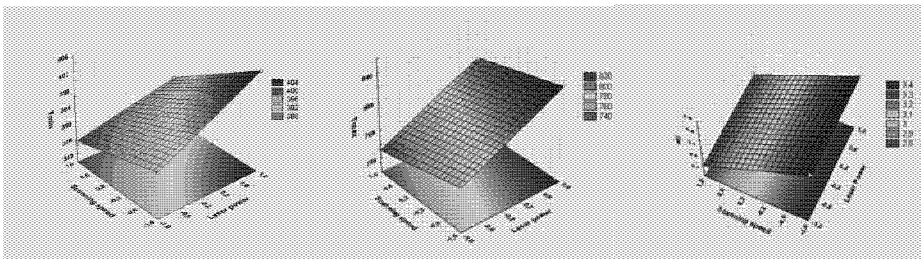
Figure 2: (a) Temperature distribution on the top surface of the petroleum fraction. (b) Temperature distribution inside of the petroleum fraction. (c) Temperature curve in the point x=0:y=0:z=0. Laser parameters of P=28W and Vs= 1.8 m/s.

Table 3: ANOVA table for maximum temperature (T_{max}), minimum temperature (T_{min}) and time models

Source	Sum of squares	df	Mean square	F-value	F-tabled 10% >F	
			Tmax model			
Model	6055.80	2	3027.90	612.99	9	Significant
P	5070.15	1	5070.15	1026.45		
Vs	985.65	1	985.65	199.55		
Residual	9.8790	2	4.939			
Cor total	6065.68	4				
			Tmin model			
Model	195.28	3	65.0965	193.93	53.59	Significant
P	85.4793	1	85.47927	254.65		
Vs	96.0498	1	96.04980	286.14		
P by Vs	13.7604	1	13.76039	40.9945		
Residual	0.3357	1	0.33566			
Cor total	195.6251	4				
			Time model			
Model	0.3821	1	0.3822	1500.97	5.54	Significant
Vs	0.3821	1	0.3821	1500.97		
Residual	0.000764	3	0.0003			
Cor total	0.382935	4				

Table 4: Summary statistics for T_{max}, T_{min} and Time models.

			Tmax variable			
Factor	**Effect**	**Std. Err.**	**t(2)**	**p**	**-90%.cnf. limt**	**+90%.cnf. limt**
Mean	783.2220	0.993933	788.0027	0.000002	780.3197	786.1243
P	71.2050	2.222502	32.0382	0.000973	64.7153	77.6947
Vs	-31.3950	2.222502	-14.1260	0.004974	-37.8847	-24.9053
R-square	0.99837					
Adjusted R-squared	0.99674					
			Tmin variable			
Factor	**Effect**	**Std. Err.**	**t(1)**	**p**	**-90%.cnf. limt**	**+90%.cnf. limt**
Mean	392.9318	0.259100	1516.526	0.000420	391.2959	394.5677
P	9.2455	0.579365	15.958	0.039841	5.5875	12.9035
Vs	-9.8005	0.579365	-16.916	0.037591	-13.4585	-6.1425
P by Vs	-3.7095	0.579365	-6.403	0.098633	-7.3675	-0.0515
R-square	0.99828					
Adjusted R-squared	0.99314					
			Time variable			
Factor	**Effect**	**Std. Err.**	**t(3)**	**p**	**-90%,cnf. limt**	**+90%,cnf. limt**
Mean	3.091920	0.007136	433.2818	0.00000	3.069210	3.114630
Vs	-0.61820	0.015957	-38.7424	0.000038	-0.668981	-0.567419
R-squared	0.99801					
Adjusted R-squared	0.99734					



(a) (b) (c)

Figure 3: (a)-(b) 3D Response surface to show effects of P and Vs on cracking T_{max} and Tmin for petroleum fraction, respectively. (c) 3D Response surface to show effects of P and V_s on time reached at T_{max} for petroleum fraction.

6. Conclusion

Temperature distribution range of a petroleum fraction from radiation laser cracking process was identified. The best range of laser parameter required to control the cracking temperature were found by the use of a full 2^2 factorial design; furthermore, the mathematical models of maximum temperature, minimum temperature and the time sample reached T_{max} were determined. Finally, the developed models are fairly accurate as the percentages of error in prediction are in good agreement.

7. Acknowledgments

This work was supported through Project 2008/08310-0 from FAPESP.

References

Celis O.J. , Tovar. L.P , Jardini A.L., Siegel C. R., Maciel Filho R, Wolf Maciel M.R., 2010, Continuous thermodynamic computational approach for correlating thermal properties of heavy and ultra heavy petroleum fractions by differential scanning calorimetry (DSC), 11th international conference on petroleum phase behavior and fouling, PETROPHASE XI, New Jersey.

Scarparo M., Kiel A., Zhiyao Z., Ferrari C., 1997, Study of resin based materials using CO2 laser stereolithography, Polymer, 99, 2175-2181.

Yongjun Shi, Hong Shen, Zhenqiang Yao and Jun Hu., 2007, Temperature gradient mechanism in laser forming on thin plates, Optics & Laser Technology, 39, 858-863. Elsevier, Shangai.H.P.