

Implication of COMSOL to Laser Powered Non-Isothermal Reactors for Pyrolysis in the Gas Phase

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Abstract

The IR CO₂ laser powered chemical conversions in the gas phase are intriguing and the researchers' attention was focused on this transformation a while ago. The method, known as Infrared Laser Powered Homogeneous Pyrolysis, or IR LPHP opened reaction pathways not reached by conventional techniques. In a LPHP reactor the energy is absorbed within a vibrational mode of the photosensitizer (mostly SF₆), and rapidly converted into heat (translational energy) via efficient relaxation processes. Energy is then transferred to the reagent molecules via collisions mostly in the same manner as in conventional pyrolysis. The small dimensions aid the rapid establishment of a steady state temperature and redistribution of reactants and products in the cell due to elimination of wall effects on the reactions. However, the calculation of temperature distribution in LPHP reactors is a complex problem, involving many factors. The application of COMSOL Multiphysics to model the temperature distribution in the gas phase in LPHP reactor opens new perspectives to accurately predict the temperature profile in horizontally or vertically aligned LPHP reactors at static and dynamic conditions. A detailed analysis of thermal conductivity of the gas media with and without thermal gaseous convection on temperature distribution was performed. Different experimental approaches such as direct thermocouple measurements, implication of "chemical thermometer" were applied to validate the COMSOL predictions.

Keywords: Lignin, Heat transfer in gases

1. Introduction

The energy production from a biomass representative lignin is an attractive option given that the higher bio-oil yields and decreased char formation are provided [1-2]. However, the detailed mechanism of lignin pyrolysis remains unclear, largely due to its complex structure and random composition [3-4]. Mass-transfer limitations on polar and higher molecular mass compounds, the influence of the surface area on the yields and kinetics for nascent compounds from pyrolysis of lignin, variation of the pyrolysis rate with sample size, thickness and the unknown character of reactions occurring during the solid phase may have a large effect on the elucidation of the lignin pyrolysis mechanism.

Therefore, it is pragmatic to convert lignin into a more high-quality bio-oil and chemicals with virtually no secondary char effects based on a method known as Infrared Laser Powered Homogeneous Pyrolysis or IR-LPHP [5-6]. The method allows to perform the pyrolysis experiments in homogeneous, "wall-less" conditions under irradiation of IR CO₂ laser and in presence of sensitizer gas SF₆. The principal advantage of this method is that all chemical processes occur only in a small "hot zone" practically at cold conditions of the reactor walls. The products of pyrolysis will diffuse out of the "hot zone" avoiding further secondary processes (degradation, cleavage, or condensation with other molecules). Different products are expected to be produced under the IR-LPHP of lignin due to the diverse heating rates, temperature, and residence times in the specific "wall-less" condition of the reactor at the same power of irradiation of the laser.

In this respect the measurement of the temperature distribution in the LPHP reactor is critical. Direct thermocouple measurements and a contactless method known as chemical thermometer were used and described as in early [5-9] as well as in our recent publications [10]. All temperature measurements have indicated that the temperature and any velocity distribution usually become steady

in a time of a few milliseconds short compared with reaction times [5-6,11].

Nevertheless, the direct measurement of temperature inside the laser beam using a thermocouple cannot be precise (because of the high dissipation rate of energy through the thermocouple material). The method of “chemical thermometer” possesses a drawback i.e. the uncertainty of the “hot zone” dimensions, necessary for the calculation of maximum temperature, increases the error bar of temperature assessments [10]. To validate all above measurements as well as to predict the value of measured maximum temperature in the laser beam depending on laser power (and other experimental conditions) a theoretical/numerical calculation was initiated which solves the traditional heat equation in cylindrical coordinates using COMSOL Multiphysics (Heat Transfer Module). The calculated temperature spatial distribution will be compared with experimental measurements in close proximity to the CO2 laser beam (the beam outside diameter - 2.5mm)

2. The Experimental Setup and The Geometry of the Model

In order to study the temperature distribution of the gas in the LPHP reactor we must first model the reactor. The LPHP reactor used in the experiment to measure the temperature has a cylindrical shape, fig.(1).

In COMSOL, it is an easy task to implement a cylindrical shape and then solve the 3D heat equation for that shape with the appropriate boundary and initial conditions. However, this approach requires a considerable amount of computational memory especially if one decides to couple the heat equation to other modules using the multiphysics node option.

One could easily overcome this difficulty by reducing the degrees of freedom solved for through the identification of symmetries in the problem. Because the reactor has a cylindrical shape and the laser propagates along the length of the cylinder, our problem is azimuthally symmetric which translates to the temperature being independent of the azimuthal angle ϕ .

Fortunately, COMSOL has the ability to implement such symmetries and reduce the degrees of freedom solved for therefore the computational size significantly. Therefore, we can model our cylinder as a rectangular 2-dimensional surface which is the cross section of an infinite plane with a cylinder, fig.(2). By solving the heat equation for the specified geometry and then rotating it by 360 degrees we get the solution for the full cylinder which agrees with solution of the 3D problem.

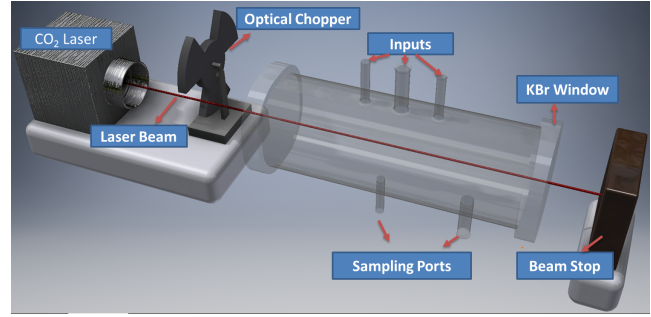


Figure 1. The experimental setup of the LPHP reactor

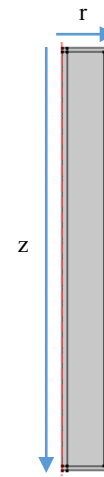


Figure 2. The rectangular shape representing the cross section of the cylinder, the blue arrows point the direction of the axis and the red line is the symmetry axis around which the object could rotate freely

3. Theory and The Governing equations

To determine the temperature distribution we utilize the heat transfer in fluids module to solve the time-dependent heat equation which is a parabolic differential equation

$$\rho(T)C_p(T)\frac{\partial T}{\partial t} - k(T)\nabla^2 T = Q \quad (1)$$

Where $\rho(T)$ is the density, $C_p(T)$ is the heat capacity at constant pressure, $k(T)$ is the thermal conductivity and Q is the heat source. As evident from Eq.(1), the thermal properties of the gas are also a function of the temperature.

The gas for which we would like to determine the temperature distribution is a mixture

of SF6 at 8.7torr pressure which approximately corresponds to 1.14% of the mixture and N2 at 98.86%. In order to model the thermal properties of the gas mixture correctly, one needs to weigh the thermal properties of SF6 and N2 with their corresponding percentage in the mixture.

$$\rho(T) = 1.14 \% \rho_{SF6}(T) + 98.86 \% \rho_{N2}(T)$$

$$C_p(T) = 1.14 \% C_p(T)_{SF6} + 98.86 \% C_p(T)_{N2}$$

$$k(T) = 1.14 \% k_{SF6}(T) + 98.86 \% k_{N2}(T)$$

$k(T)$ and $C_p(T)$ are inputs of the model.

They are constructed as piecewise functions in COMSOL by utilizing the built in functions for SF6 and N2 from the material library. However, $\rho(T) = M_n p_A / RT$ is an output of the model and is taken to be the density of the mixture when it is treated like an ideal gas and depends only on M_n the molar mass of the mixture as an input and is weighed the same way as the density. The ideal gas assumption is accurate since there are no interactions between the SF6 and/or N2 molecules and the heat distribution is due to the thermal chaotic motion of the SF6 molecules.

In order to model the laser source responsible for the heating of the gas in the LPHP reactor we choose the heat source to be $Q = -\frac{dI}{dz}$ where $I(z)$ is the laser intensity and is a function of the propagation direction z .

Since the heating of the gas is due to absorption of the laser energy by SF6 molecules, it is appropriate to use the Beer-Lambert law $I(z) = I_0 e^{-\mu(T)z}$ [12] to describe the behavior of the laser intensity as it travels in the gas mixture along the length of the LPHP reactor. Therefore $Q = -\frac{dI}{dz} = \mu(T)I(z)$ is determined by utilizing the General Form PDE module and solving for $I(z)$.

The absorption coefficient $\mu(T)$, is also constructed by weighing the absorption coefficients of SF6 and N2. In our model, we take the absorption coefficient of N2 to be constant because according to [13] it is independent of the temperature for wavelengths of the visible spectrum and is equal to $10^{-2} \frac{1}{cm}$. As for the absorption coefficient of SF6, we fit a mathematical function, fig.(3), to measured data points from [14-15].

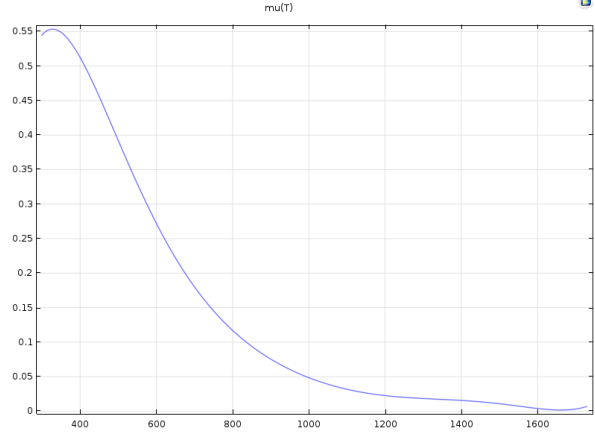


Figure 3. The absorption coefficient (1/cm) as a function of the temperature (K) fitted to [14-15]

The equation at hand for $I(z)$ is a first order differential equation which implies that the solution to it is determined up to a constant. To find this constant one needs to apply appropriate boundary conditions. For the sake of this calculation, we implement a Dirichlet boundary condition at the entrance of the cylinder

$$I(z) = 0.9I_0 e^{-r^2/\sigma^2} \quad (2)$$

Where 0.9 accounts for the transmitted laser intensity, σ is the radius of the laser beam and $I_0 = P/\pi\sigma^2$ is the initial intensity at the entrance and $P = 6.6W$ is the power of the laser beam. Equation (2) is chosen such that the laser Intensity will have a Gaussian profile along the radius of the cylinder.

The heat loss through the cylinder is accounted for through grey body radiation on the surface and through natural air convection. The heat transfer coefficients for both cases were used from the built in library of COMSOL.

4. Meshing

Physics controlled meshing was used with an extremely fine mesh. Because of the symmetry implementation the calculation approximately takes 10 seconds on a MacBook Pro laptop which is extremely fast. This further illustrates the power of COMSOL and its ability to implement symmetries that reduce the degrees of freedom. Different calculations with different element sizes show convergence of results at the level of fine meshing.

5. Results

We solve the time dependent solver for different laser powers by utilizing the parametric sweep option which allows to run the calculation for different values of the same parameter. Below we show some of the images and the plots obtained

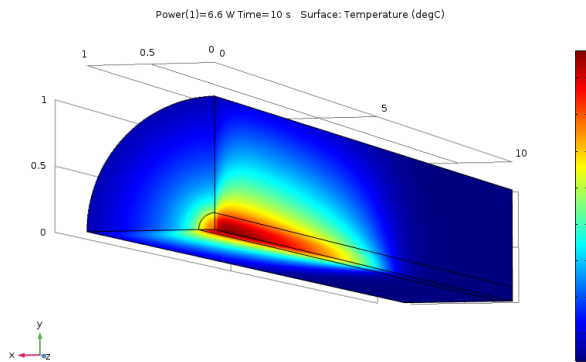


Figure 4. The surface temperature (degC) of a quarter of the cylinder at time=10s and laser power=6.6W

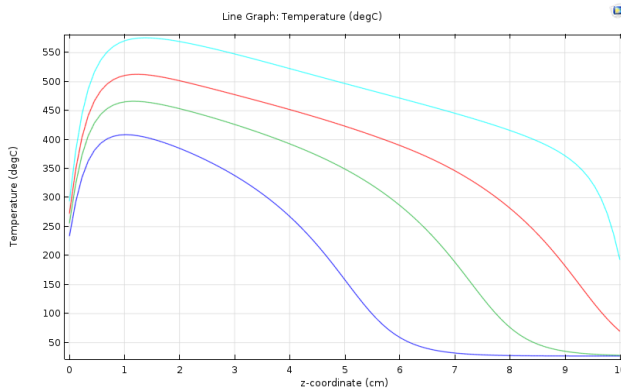


Figure 5. The temperature (degC) as a function of z(cm) when $r=0.4$ cm for different laser powers, 6.6W(blue), 10.8W(green), 15W(red) and 22W(cyan)

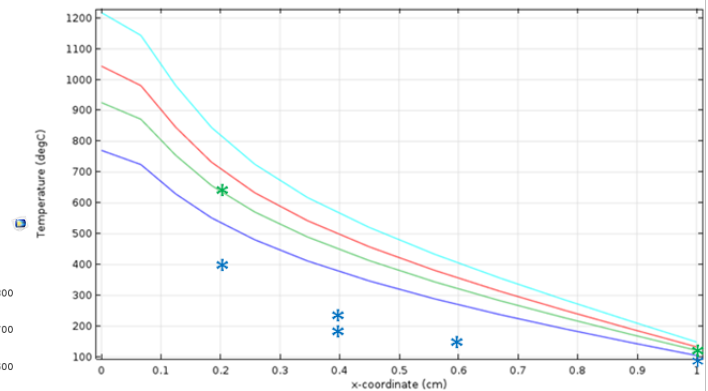


Figure 6. The temperature (degC) as a function of x(cm) when $z=2.2$ cm(the location where thermocouple measurements were taken) for different laser powers, 6.6W(blue), 10.8W(green), 15W(red) and 22W(cyan). The dots represent the experimental measurements for 6.6W(blue) and 10.8W(green) laser powers

Conclusions

It seems COMSOL accurately predicts the temperature distribution of SF₆ in a IR LPHP reactor. The results from the COMSOL simulations are in a fair agreement with the experiment. We believe the slight disagreement is due to neglecting the internal convection of the gas mixture. We believe the implementation of internal convection should drop the temperature. COMSOL has the ability to implement this through coupling the Laminar flow module to the Heat transfer module and solving for a Non-isothermal flow. However, since the LPHP reactor was placed horizontally the gravity acts along the x(or y) direction. This destroys the azimuthal symmetry and therefore requires to solve the problem in 3D which in turn demands huge computational memory and is impossible to do on a desktop computer.

In the near future, we would like to parallelize our problem and run it on a supercomputer and fortunately COMSOL has the ability to carry this out.

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