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AN OVERVIEW OF SOLAR THERMAL CRACKING OF NATURAL GAS: CHALLENGES AND SOLUTIONS TOWARDS COMMERCIALIZATION

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ABSTRACT

Solar thermal cracking of natural gas has great potential to become an attractive alternative process for hydrogen and carbon black production due to its zero emission footprint. However, there are two major problems preventing this process from commercialization: **(1)** carbon deposition causing reactor clogging, **(2)** intrinsic losses in energy conversion efficiency as a result of re-radiation losses and inherently transient nature of the solar energy. The second problem in particular applies to all types of solar reactors despite the reactants and products because temperature has the most important impact on reactant to product conversion efficiency. This paper provides a detailed description of these two problems, and summarizes few solutions addressing these challenges.

INTRODUCTION

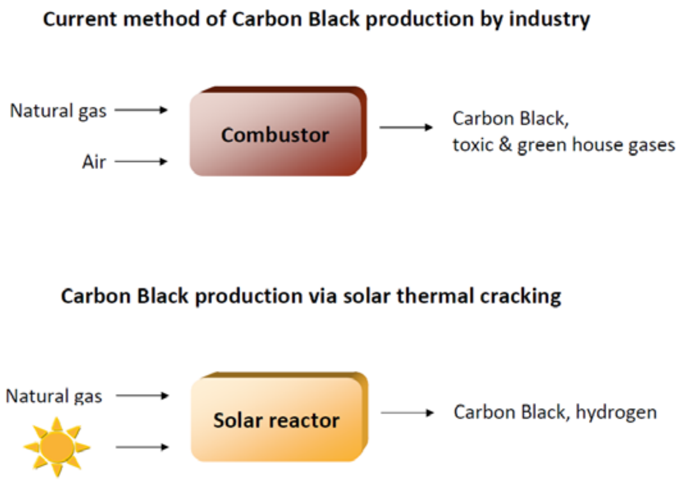
Solar thermal decomposition of natural gas, or "solar cracking", offers a great alternative to traditional ways of hydrogen and carbon black production in industry [1]. In order to produce hydrogen and carbon black via solar cracking, a solar reactor is needed to house the high temperature chemical process. By placing the solar reactor in the focal point of an optical solar concentration system, intermittent solar energy is converted into storable chemical energy.

Hydrogen and carbon black production via solar cracking of natural gas is an endothermic reaction occurs as follows:

$$CH_4 \rightarrow C + 2H_2, \quad \Delta H = 75 \text{ kJ/mol} \qquad (1)$$

Carbon and hydrogen produced from this process can be used both as a commodity and fuel. For example, hydrogen is a crucial commodity in petroleum industry for refining of crude oil via hydrocracking and hydro treatment processes. As for the carbon black, due its wide-range use, such as in car tires, batteries, conveyer belts, polymers etc., it is basically the most important technical carbon product after metallurgical coke.

Currently, the most practiced way of hydrogen production in industry is steam reforming of natural gas, which emits large amount of green house and toxic gases [2]. On the other hand, carbon black is mainly produced via furnace process, which is also responsible for large amount of hazardous gas emissions and serious health problems for the workers of carbon black industry [3]. Because of environmental and health wise harmful impacts of these production techniques, there has been a lot of interest on finding cleaner methods for hydrogen and carbon black production. Considering the zero emission footprint of solar cracking process, production of these two important commodities can be done in one process without taking any harmful impacts on the environment and human health. We can illustrate the comparison of hydrogen and carbon black production by industry vs. hydrogen and carbon black production via solar cracking in a simplified flow diagram as shown in Figures 1 and 2.



Current method of Carbon Black production by industry

Carbon Black production via solar thermal cracking

Figure 1 Carbon black production by industry vs. via solar cracking

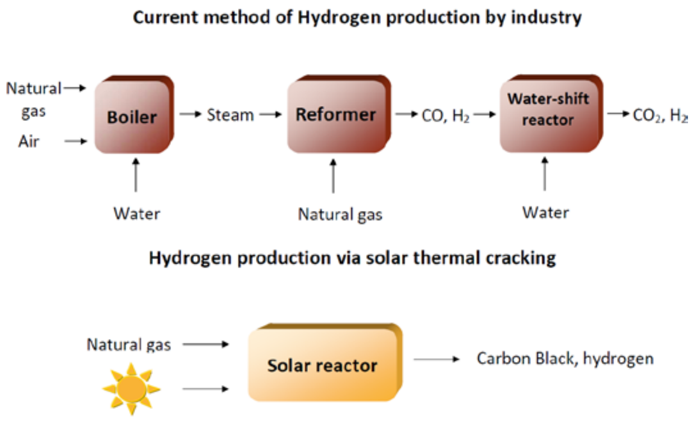


Figure 2 Hydrogen production by industry vs. via solar cracking

As it is seen in Figures 1 and 2, solar cracking of natural gas yields with both of these valuable products at a time without any emissions. However, there are two major challenges preventing this striking process from commercialization:

1. Carbon particle deposition on solar reactor window, reactor walls, and reactor exit.
2. Variations in solar radiation due to weather conditions, and the position of the sun.

Especially the first problem leads to reactor clogging due to excessive deposition of carbon particles at the exit. As for the second problem, it is a common problem for any solar reactor processing solar thermochemical reaction. Although these two problems are completely independent from each other and need to be addressed separately, there is one common aspect in these problems: that they can be solved by focusing on the reactor design. This paper summarizes our research efforts yielding successful solutions to these two problems that have been numerically proven to be successful.

CARBON DEPOSITION AND REACTOR CLOGGING

Upon the decomposition of natural gas into hydrogen and carbon inside the solar reactor, carbon particles tend to move towards reactor window and deposit on the quartz window. The rest of the carbon particles either deposit on reactor walls or move towards the exit all together. Carbon deposition on the quartz window blocks the incoming solar radiation and therefore drops the temperature inside the reactor. As for the deposition at the exit, those carbon particles agglomerate and completely block the exit causing the reactor to explode.

All of the natural gas carking solar reactors suffer from carbon deposition and clogging problem. For example, Abanades and Flamant observed that carbon particles adhere to the walls and tapering the nozzle, which made them to conclude that one of the major challenges in designing a solar cracking reactor is to solve the carbon deposition problem [4]. Kogan group of Weizmann Institute of Science achieved an effective way of window screening. However, although the window was kept reasonably clean from carbon deposition, carbon particles still deposited on the walls and at the exit [5].

In order to explain carbon deposition inside solar reactor, we previously took Kogan group's experimental results presented in Ref. [6] as a reference case for "clean window" and "contaminated window" to see if we could computationally predict these results and therefore explain the physics behind this phenomenon [7]. We used Discrete Phase Model (DPM) to evaluate trajectories of carbon particles and to track them through continuous phase of gas. We got the motion of particulate phase based on force balance equating particle inertial forces on a Lagranian frame of reference with the forces acting on the particle. Our simulations successfully predicted the contaminated window and clean window experiments of Kogan group as shown in Figures 3.

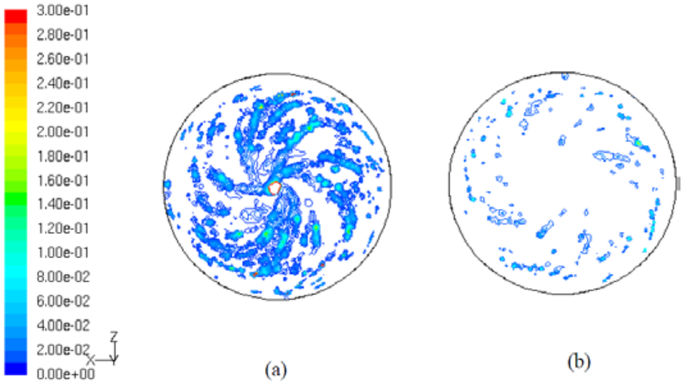


Figure 3 (a) Significantly contaminated window, (b) Slightly contaminated window

Although Kogan et al. presented window contamination, they did not give information on reactor wall contamination. Since we successfully predicted their experimental findings for the clean window case and contaminated window case, we went ahead and predicted the carbon deposition at reactor exit for these cases. As shown in Figure 4(a), significant carbon deposition is observed at the exit, whereas slight carbon deposition is observed in Figure 4(b) for the case where slight carbon deposition is observed for the window as well.

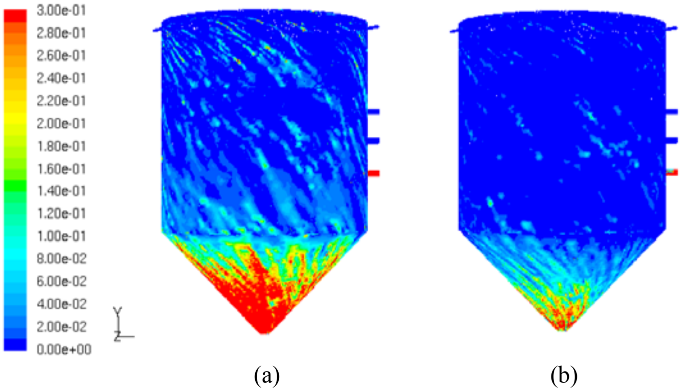


Figure 4 (a) Significant carbon deposition at reactor exit, (b) Slight carbon deposition at reactor exit

Therefore, we can say that experimental case where they got almost a clean window; they probably had a cleaner exit than the case when they had a contaminated window.

Upon the completion of our simulations for the carbon deposition at the reactor exit, we merged our simulation code with visualization tool EnSight, which gave us a three-dimensional animation of this striking process on a stereoscopic 120° curved screen showing images as large as 3576 x 1024 pixels. The three dimensional immersive visualization elaborated the phenomenon of solar cracking natural gas into carbon black and hydrogen molecules when solar radiation hits the natural gas inside the reactor.

With this animation, we were able track the carbon particles and clearly observe temperature variations inside the reactor in the three dimensional domain, but were also able to observe the changes in flow behavior. Figure 5 shows snapshots of our three dimensional video illustrating solar reactor explosion because of carbon particles accumulation at reactor exit.

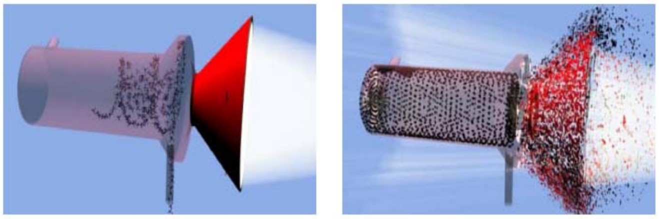


Figure 5 Carbon blockage exploding the solar reactor

The computational tasks in this work were performed using the supercomputer facilities of Texas A&M University at Qatar (TAMU-Q), where 512 cores cluster housed in 64 nodes, which are connected together through a 20 Gbps infiniband network.

SOLUTION TO REDUCE CARBON DEPOSITION

We have approached to this problem by investigating the flow behavior inside a solar reactor for this two-phase thermochemical reaction. In order to understand the flow behavior and track the carbon particles inside the reactor, we have applied our successful CFD model to our aero-shielded reactor concept shown in Figure 6.

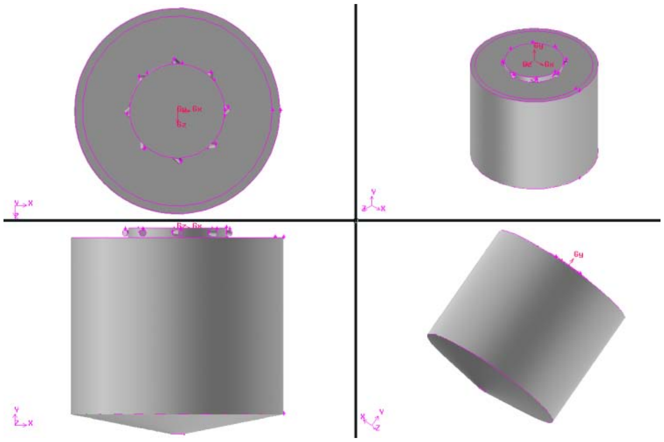
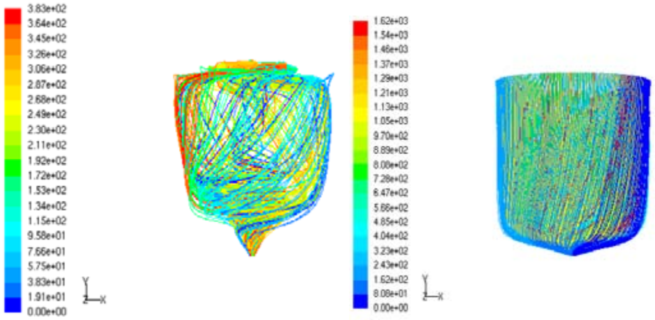


Figure 6 Aero-shielded solar cyclone reactor

The three-dimensional geometry for simulations is built using GAMBIT, which is also used for generating the non-uniform unstructured grid in the geometry. The basic geometry with flow conditions and the adapted grid used for simulations is shown in Figure 7, where the details of the CFD model can be found elsewhere [7, 8, 9].

Figure 7 Meshed geometry

In this reactor concept, natural gas main flow is injected through impeller disk jets from the top center of the reactor with a 45° angle at a flow rate of 7m/s creating a strong vortex concentrated in the middle of the reactor. With this reactor configuration, we obtained a laminar flow shield covering the interior walls of the solar reactor as shown in Figure 8(a) and strong vortex-or cyclone-in the core as shown in Figure 8(b).



(a) (b)

Figure 8 (a) Vortex flow inside the solar reactor, (b) Aero-shield on the solar reactor walls

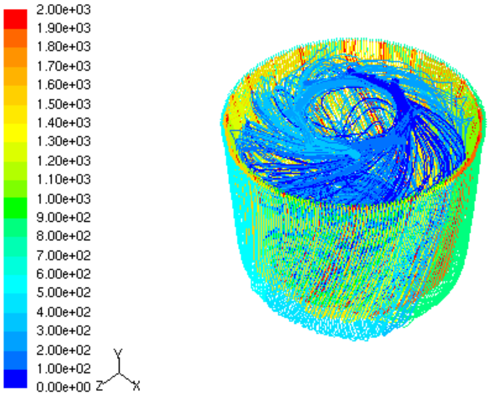


Figure 9 Isometric view of the solar reactor

The laminar flow shields the reactor walls like a shower keeping carbon particles away; hence it is called "aero-shielded". The laminar flow serving as aero-shield and the vortex flow do not disturb each other as it is seen in Figure 9. The vortex flow in the core generally increases residence time forcing the carbon particles to circle inside the reactor couple times before heading towards the exit. Since the carbon particles do not move towards the exit all at once, this flow pattern reduces the clogging problem [10].

INTRINSIC LOSSES IN ENERGY CONVERSION DUE TO TRANSIENT NATURE OF SOLAR ENERGY

Re-radiation losses and inherently transient nature of the solar energy are the main reasons for intrinsic losses in energy conversion in any solar reactor. When solar energy enters into reactor as a source of high temperature process heat; incident radiation needs to be concentrated over a small surface area, the inlet of which is called the "aperture". The image of incoming solar radiation over the aperture can be approximated by a Gaussian distribution where the solar radiation inside the reactor varies by the peak value and aperture size. However, because of the transient nature of solar energy, there is a critical need for proper control to maximize system efficiency under field conditions.

Up to date, all solar reactors have been made on the assumption of homogenous and instantaneous temperatures inside solar reactor, e.g. fixed aperture. Although there have been studies on the effect of different aperture size [11], and on the effect of intermittent insolation on the conversion rate [12], aperture size has always been kept constant in solar thermochemical reactors.

It should be noted that intermittence in the incident flux entering the reactor is a product of the environment, geometrical design of the concentration system, tracking algorithms and overall concentration ratios. Furthermore, wear and fouling of concentration surfaces and of the aperture window also affect maximum achievable flux densities. These factors combined are present within any solar concentrator and each serve to decrease efficiency. Therefore, it is important to design a system that allows the reactor to respond to environmental factors in order to maintain semi-constant temperatures inside the reactor [13].

SOLUTION TO CONTROL INTRINSIC LOSSES

It is important to keep the reactor temperature constant so that the process efficiency remains constant regardless of weather conditions. In order to do that, a variable aperture sensible to changes in weather would help in maintaining semi-constant temperature inside the solar reactor.

By determining the output of the reactor with a dynamic aperture and changing flux conditions, we can see the impact of variable aperture size. We know that the absorption efficiency is the ratio of "difference in how much power is intercepted by the aperture and how much power is reradiated through the aperture due to the cavity temperature" to "the total amount of power reflected towards the reactor by the concentration system" as shown in Eq. (2):

$$\eta_{absorption} = \frac{\alpha_{eff} P_{aperture} - \varepsilon_{eff} A \sigma T^4}{P_{in}} \qquad (2)$$

where α_{eff} and ε_{eff} are the effective absorptance and emittance of the receiver, $P_{aperture}$ is the amount of power intercepted by the aperture, P_{in} is the total power reflected by the concentration system, A is the aperture area, σ is the Stefan-Boltzmann's constant, and T is the internal temperature of the cavity. The energy used during the chemical decomposition of methane is defined as the product of the required change in enthalpy and the mass flow rate. Convective losses can be modeled based on a desired isothermal temperature and room temperature environmental operating conditions under natural convection. Internal wall temperatures can be considered as the same temperature of the cavity temperature. Heat is conducted through the cavity, through the insulation, and then dispersed through natural convection. Based on this model, which is described elsewhere in detail [10], variable aperture size indeed help in maintaining semi-constant temperature inside a solar reactor.

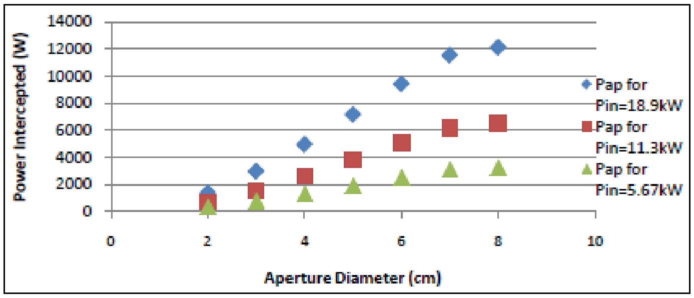


Figure 10: Aperture diameter vs. power intercepted

For example, if we want to capture let's say 4kW power inside the reactor regardless of changes in weather conditions, we can refer to Figure 10 to find out what should be the aperture size. If the incoming power is 18.9kW, we need to shrink the aperture size to 4cm approximately. Or if the incoming power is 11.3kW, then the aperture size should be approximately 6cm to capture 4kW. If the incoming power is too low because of clouds or dust storm etc., such as 5.67kW, then the aperture size should be enlarged to 10cm approximately to capture 4kW. This sequence shows us that by changing the aperture size according to the changes in the incoming solar flux, we can maintain semi-constant conditions inside the reactor.

It should be noted that, the aperture, by definition, is at the entrance to the reactor and will experience a high degree of solar influx. Active cooling would be needed in order to maintain operational capabilities when the aperture is occluding a large part of the concentrated solar power.

It should also be noted that some of the incoming radiation will be lost when the aperture size is changed. However, what is more valuable than intercepting the maximum amount of radiation is maximizing the net amount of energy transferred into the reactor. The variable aperture allows the reradiation energy to be modulated at a cost of intercepted energy. The exact aperture size is dependent on the distribution and intensity of the concentrated solar radiation, desired internal temperature, and actual internal temperature. Because of these temperatures, reradiation losses, depending on aperture geometry, will take precedence over conductive and convective losses, where the radiation losses are proportional to the aperture area and internal temperature to the fourth power.

Therefore, efficiency is enhanced because controlling the aperture enables the control of reradiation losses and intercepted radiation. At some point, again depending on the total concentrated flux intensity, distribution, and aperture size, there is a maximum amount of net power available. This maximum changes as the flux intensity changes, e.g. because of weather, fouling, etc. By changing the aperture size, we can maintain, or more closely follow, the maximum efficiency throughout various operating conditions.

If we take a look at the impacts of this mechanism on solar cracking of natural gas to produce hydrogen: essentially the hydrogen production is bounded by the net power received by the system minus the convective and conductive losses. The general end goal of solar thermal cracking research is to provide an alternative approach to traditional hydrogen gas production methods. Therefore, variable aperture mechanism may offer a good alternative to maintain semi-constant hydrogen production with zero emissions regardless of weather conditions, except for during the night of course.

Once completed our CFD and Optics simulations, we created three dimensional animation of the variable aperture mechanism for the solar reactor as shown in Figure 11.

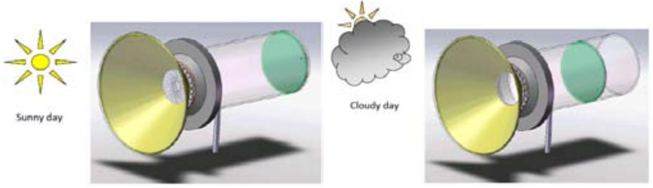


Figure 11 Variable aperture mechanism

This figure shows that in a sunny day, aperture shrinks whereas it enlarges in a cloudy day. This concept has been inspired from human eye's pupil, which shrinks and dilates in proportion to the light falling on it.

CONCLUSIONS

Two major problems of solar cracking reactors were presented along with some solutions. A new mechanism to increase the efficiency of a solar thermal cracking system and another potential solution to one of the problems facing solar reactors, e.g. carbon clogging, were described. It is certainly up to industry to decide if they like what we propose vs. what they currently practice to produce hydrogen and carbon black.

In summary, the findings of this research can be outlined as follows:

- Carbon deposition can be reduced by implementing a laminar wall screening and a vortex flow inside the reactor.
- Semi-constant temperature inside the reactor can be achieved by variable aperture concept.
- Active cooling would be needed in order to maintain operational capabilities when the aperture is occluding a large part of the concentrated solar power.
- Efficiency is enhanced because controlling the aperture enables the control of reradiation losses and intercepted radiation.
- The exact aperture size is dependent on the distribution and intensity of the concentrated solar radiation, desired internal temperature, and actual internal temperature.
- Hydrogen production is bounded by the net power received by the system minus the convective and conductive losses, therefore, via this variable aperture concept, it is possible to obtain semi-constant hydrogen production rate regardless of weather conditions.

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