

## Development of Reaction Kinetics for Diesel-Based Fuel Cell Reformers

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### Abstract

Single component as well as binary component reforming studies were conducted on diesel surrogates (tetradecane, decalin, and 1-methylnaphthalene). H<sub>2</sub>, CO, and CO<sub>2</sub> production was measured as a function of temperature, space velocity, and reforming type for a Pt-based catalyst. Intermediate species formation of various hydrocarbons including olefins and aromatics were observed during reforming. The H<sub>2</sub> production rates at the same conditions were observed in this order: Aromatics << Naphthenes < Paraffins. In binary component studies, overall yields were not additive of yields from individual fuel components. Relative reactivity of one fuel component considerably affects the conversion pattern of other; the more the difference in relative reactivity; the larger the effect. Partial oxidation reforming was affected significantly by the difference in the reactivity of fuel components; highly reactive component consumes available O<sub>2</sub> and produces combustion products. Whereas, O<sub>2</sub> is not spared for the less reactive component; pyrolysis reaction dominates.

### Introduction

Fundamental understanding for design and operation of reformers is important for successful technology development. One of the most fundamental engineering design parameters that can be measured in the laboratory is the intrinsic kinetics of a catalyst system. Once established for a particular feedstock and catalyst system, they can be coupled with computational fluid dynamics (CFD) code to effectively design, optimize, and minimize hydrocarbon slip in ATR systems. In principle, the kinetics of NO<sub>x</sub> formation, sulfur poisoning, carbon formation, and catalyst aging can be added to allow for a complete predictive model for reformer performance and operation.

However, modeling of reforming systems is extremely complicated. Diesel fuel consists of a complex variable mixture of hundreds of hydrocarbon compounds containing mainly of olefins, saturates and aromatics. Empirical expressions for space velocity or simple

power law-type models are typically used to design reformers. Unfortunately, these tend to be limited to a specific catalyst, fuel composition, and operating point. Hence, the development of validated predictive models that can account for variations in these parameters would be beneficial.

For the ATR of diesel with steam and O<sub>2</sub>, a complex reaction network is expected. Elucidation of this network and the development of a generalized complex network model for platinum catalysts is the initial focus of this work.

## Experimental

A fixed bed reactor system was used to conduct the experiments. The reactor was operated continuously at steady state.  $\gamma$ -Alumina supported platinum (0.611 wt%) catalyst (surface area 103 m<sup>2</sup>/g) was used in this study as a base catalyst. A summary of reaction conditions is given in Table 1.

Individual model compounds representing each organic class in diesel were subject of autothermal (ATR), partial oxidation (POX), and steam reforming (SR) at temperature and space velocity ranges given in Table 1. n-Tetradecane (TD), decalin or decahydronaphthalene (DHN), and 1-methylnaphthalene (MN) were identified as model compounds to represent paraffins, naphthenes, and aromatics, respectively, found in diesel. Similar studies were also conducted with a mixture of two model compounds from different hydrocarbon classes, e.g. one from aromatics and one from paraffins, to understand the combinatorial effects of feed components. A rotatable-central-composite design was used for process optimization.

**Table 1.** Experimental conditions

	ATR	SR	POX
O <sub>2</sub> /C	0.3	0.0	0.5
H <sub>2</sub> O/C	1.5	3.0	0.0
T (°C)	750 – 900	750 – 850	750 – 850
GHSV (h <sup>-1</sup> )	50,000 - 200,000 20,000 - 65,000*	50,000 - 200,000 20,000 - 65,000*	50,000 - 200,000 20,000 - 65,000*

\*If 1-methylnaphthelene is in feed

Gas chromatographs were used to identify and separate the reaction products. Also, a GC/MS was used to quantify and identify the complex liquid hydrocarbon product mixture that formed at various hydrocarbon conversions. Product yield is reported as a percentage of the theoretical yield based on moles of carbon in hydrocarbon fed to the reactor. For example, the yield of product A (H<sub>2</sub>, CO, and CO<sub>2</sub>) can be defined as,

$$\text{Yield of A (\%)} = \frac{\text{Moles of A produced}}{N \times \text{moles of hydrocarbon fed to the reactor}} * 100$$

Where, N is the number of carbons in hydrocarbon fuel used in this study. In some cases, H<sub>2</sub> yields may be higher than 100% since SR and WGS reaction also contributes in H<sub>2</sub> production apart from hydrocarbons.

## Results and Discussion

### Statistical Analysis of Reforming Process

To select an appropriate model, it is necessary to understand the reaction mechanisms and pathways for the chemical system. One approach to gaining that understanding is surface response mapping. This is a statistical technique used to map characteristic responses (e.g. yield, conversion, carbon buildup, etc.) to input variables ( $O_2/C$ ,  $H_2O/C$ , temperature, space velocity, etc.) over a defined region. It identifies the significance of parameters and their interactions. Also, it provides data that can lead to validation of kinetic models and to test the statistical significance of proposed reaction pathways. As the most important mechanisms and reaction pathways are defined, appropriate models can be selected to develop a model. This is initially being done for a Pt catalyst and will be extended to other catalyst systems as needed.

The yields of individual species from hydrocarbon reforming,  $z$ , which depend on the space velocity ( $x$ ) and reaction temperature ( $y$ ), can be described by the equation

$$z = b_0 + b_1x + b_2y + b_{11}x^2 + b_{22}y^2 + b_{12}xy \quad (1)$$

where  $z$  = the yield of individual species after completion of the reaction,  $x$  = gas hour space velocity ( $hr^{-1}$ ),  $y$  = temperature (K), and  $b_0 \dots b_{22}$  are the coefficients of the model. The coefficients of Equation 1 were estimated by making use of the responses of experiment for the standardized values of  $x$  and  $y$  which varied in the range given in Table 1. A relationship between yields ( $z$ ) and two quantitative variables  $x$  (space velocity) and  $y$  (reaction temperature) is represented by response surface curve as shown in Fig 1-5. Coefficients of quadratic Equation 1 are summarized in Table 2 for  $H_2$  and CO yields from ATR of different individual model compounds used in this study. Quadratic fit of data from response surface mapping was excellent (>90%).

**Table 2.** Coefficients of quadratic equations for ATR of model components

Fuel	X	Coefficients						$R^2$
		$b_0$	$b_1$	$B_2$	$b_{11}$	$b_{12}$	$b_{22}$	
TD	$H_2$	1313.8	$-5.953e^{-4}$	-2.3644	$1.442e^{-9}$	$-1.418e^{-7}$	$1.159e^{-3}$	0.96
	CO	283.8	$2.888e^{-4}$	-0.6240	$7.44e^{-10}$	$-6.302e^{-7}$	$3.86e^{-4}$	0.98
MN	$H_2$	1155.9	$1.9043e^{-3}$	-2.3600	$4.659e^{-9}$	$-2.4403e^{-6}$	$1.225e^{-3}$	0.98
	CO	521.8	$1.7130e^{-3}$	-1.1354	$-6.07e^{-10}$	$-1.6161e^{-6}$	$6.15e^{-4}$	0.96
DHN	$H_2$	657.4	$-2.608e^{-4}$	-1.4708	$2.658e^{-9}$	$-4.198e^{-7}$	$8.66e^{-4}$	0.97
	CO	1975.2	$-1.1579e^{-3}$	-3.6676	$1.718e^{-9}$	$-6.685e^{-7}$	$1.738e^{-3}$	0.87

Different hypothetical reaction schemes of the process are established based on the response surface methodology studies. Each of the proposed kinetic schemes is being evaluated with respect to the experimental results using an iterative predictor-corrector method based on the Himmelblau-Jones-Bischoff technique [1, 2]. Following criteria are being utilized to assess the validity of model: calculated rate constants (positive values and follow Arrhenius Law), minimized value of objective function, and calculated profile of species concentration variations.

### Individual Model Component Studies

Model compounds representing each homologues series present in diesel were evaluated to develop surface response maps for SR, POX, and ATR over Pt catalysts. Each model compound behaved differently upon reforming under the same conditions. Aromatics were less active than aliphatics and required relatively higher contact time to convert into synthesis gas. The H<sub>2</sub> production rates at the same conditions were observed in this order: Aromatics << Naphthenes < Paraffins.

Hydrocarbon product distributions depended greatly on the model compound, type of reforming performed, and the process parameters (space velocity and reaction temperature). Generally, in addition to desired products (H<sub>2</sub> and CO), the gas product streams also include CO<sub>2</sub>, C1 to C7 n-alkanes, ethylene, propylene, and benzene. CH<sub>4</sub> and CO<sub>2</sub> were the major by-products present in the significant amounts in the gas product streams. Furthermore, a series of oxygenated products such as aldehydes and ketones were observed in liquid product from POX of TD, particularly at higher space velocities and lower temperatures. Also, a series of  $\alpha$ -olefins and several isomers of tetradecene were observed in the liquid product stream from ATR and POX of TD.

Figs 1-3 show the effect of temperature and space velocity on the yields of H<sub>2</sub>, CO, and CO<sub>2</sub> from the ATR of TD. Figs 4-5 show the yields of H<sub>2</sub> from the ATR of MN and DHN, respectively. Generally, the yields of H<sub>2</sub> and CO increased with increasing reaction temperature and decreasing space velocity. However, the yields of CO<sub>2</sub> from ATR of TD and DHN decreased with increasing temperature, because the lower temperatures favor the WGS reaction; while the reverse of WGS reaction facilitates at higher temperatures.

Higher yields of CH<sub>4</sub> (1-10%) were observed in the product gas from ATR of different feedstocks. CH<sub>4</sub> is not thought to be produced from the methanation reactions because those reactions are not thermodynamically favored at the temperature studied. It is probable that CH<sub>4</sub> is formed by successive  $\alpha$ -scission of the hydrocarbons on the metal catalysts,



Higher yields of methane compared to negligible other hydrocarbons coupled with the significant concentrations of naphthalene in the product stream from ATR of MN suggests that the reforming of aromatics starts with a dealkylation reaction.

Yields of cracking products, lower paraffins and olefins, decreased as temperature increased or space velocity decreased. Higher temperatures facilitate the cracking reaction, but at the same time it also increases the rate of reforming reaction. Increasing the residence time would increase the contact time between the catalyst and reactants and, hence, the conversion of cracking products into syngas is also relatively higher, which makes the yield of cracking products lower.

Isoparaffins or branched olefins were not observed, which suggests that isomerization reactions are not taking place during reforming of diesel fuel components. Also, naphthenes were not detected from the ATR of paraffins or aromatics. However, a series of olefins (alkenes, dienes, trienes, alkynes, etc.) formed from reforming of TD particularly at higher space velocities and lower temperatures.

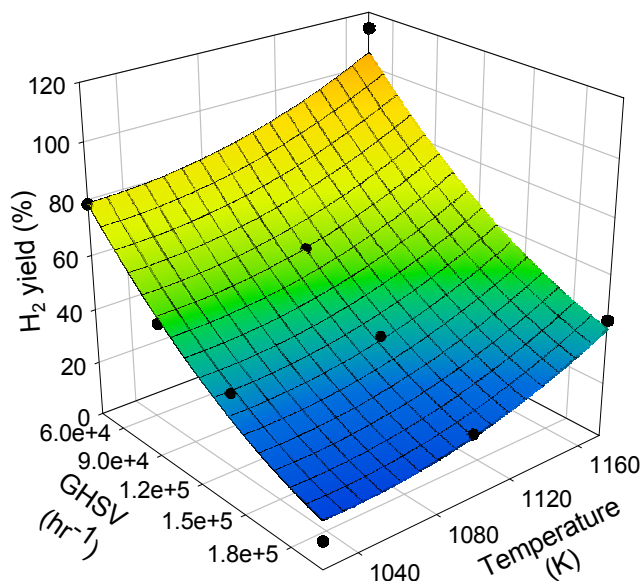


Fig 1. Yield of H<sub>2</sub> from ATR of TD(O<sub>2</sub>/C=0.3 and S/C=1.5

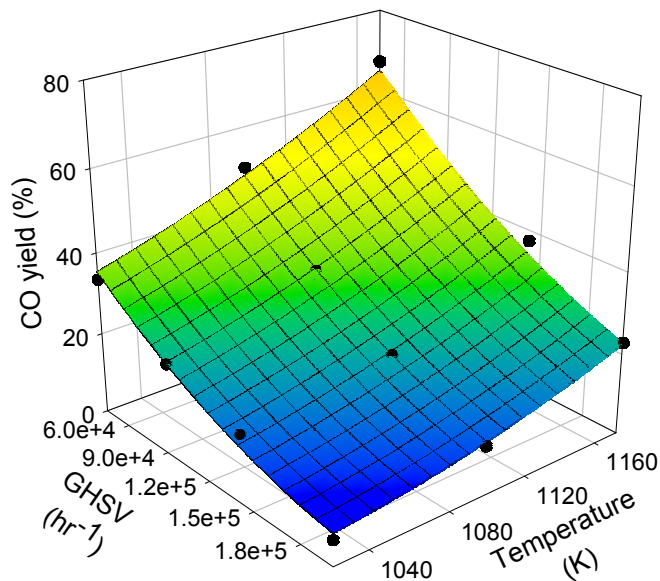


Fig 2. Yield of CO from ATR of TD(O<sub>2</sub>/C=0.3 and S/C=1.5)

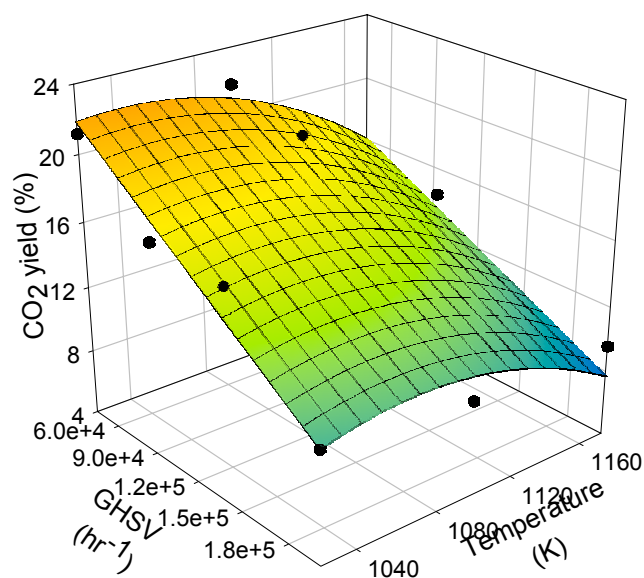


Fig 3. Yield of CO<sub>2</sub> from ATR of TD(O<sub>2</sub>/C=0.3 and S/C=1.5)

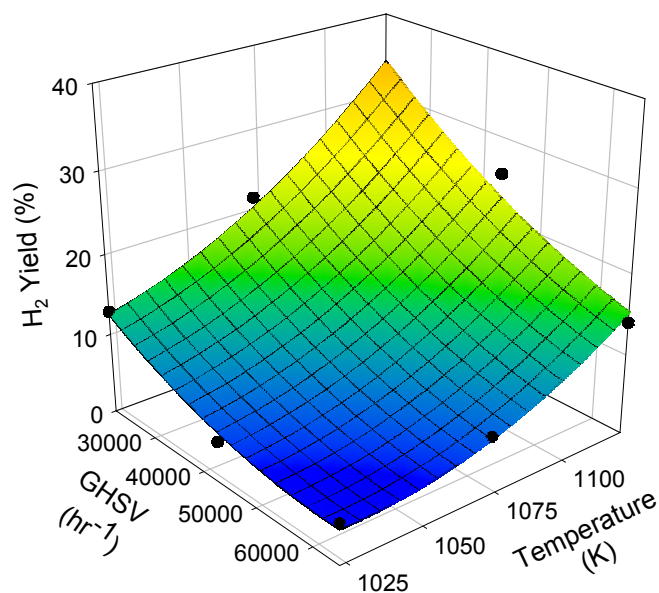


Fig 4. Yield of H<sub>2</sub> from ATR of MN(O<sub>2</sub>/C=0.3 and S/C=1.5)

Production of olefins and aromatics were significant from ATR as well as POX of TD at higher space velocity and temperature. Formation of compounds such as n-octylbenzene but no naphthenic compounds from the paraffin reforming suggests that the aromatics are produced primarily by cyclization reactions of poly-enes rather than cyclization of paraffins to naphthenes and then dehydrogenation to aromatics. Reforming of DHN also produced significant concentration of aromatics presumably via dehydrogenation reaction.

Reforming of MN at elevated temperatures (~900 °C) produced significant coking on the catalyst and resulted in higher pressure drops and eventually reactor plugging. Aromatics

contribute significantly to the catalyst deactivation compared to paraffins and cycloparaffins present in the diesel fuel.

### Binary Fuel Compound Studies

Binary fuel compound studies were conducted to understand the combinatorial effects of feed components. Therefore, surface response maps were developed for SR, POX, and ATR over Pt catalysts for three binary fuel mixtures (TD + MN, DHN + MN, and TD + DHN). Figs 6-8 show the effect of temperature and space velocity on the yields of H<sub>2</sub>, CO, and CO<sub>2</sub> from the ATR of MN + TD. Figs 9-10 show the yields of H<sub>2</sub> from the ATR of MN + DHN, and TD + DHN, respectively.

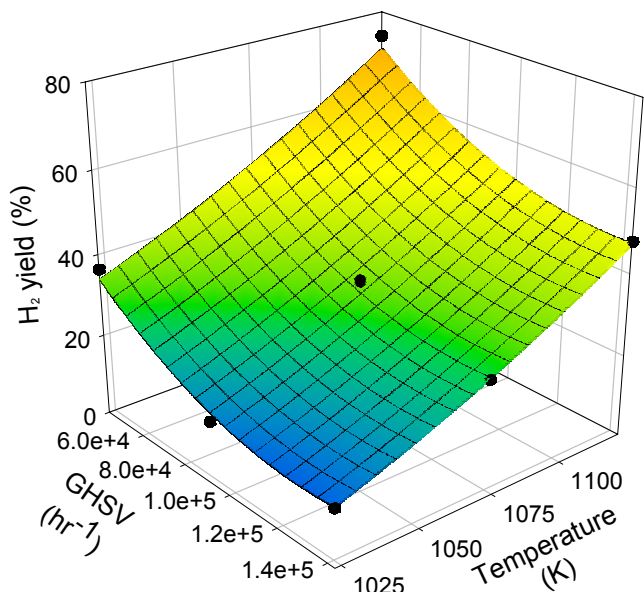


Fig 5. Yield of H<sub>2</sub> from ATR of DHN(O<sub>2</sub>/C=0.3 and S/C=1.5)

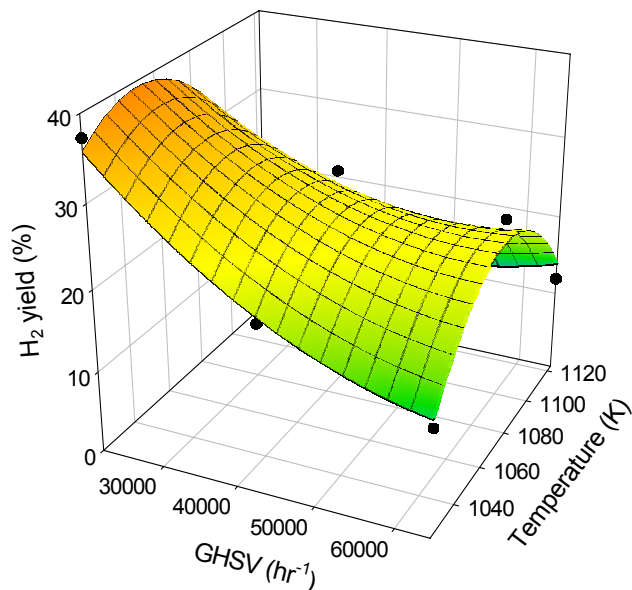


Fig 6. Yield of H<sub>2</sub> from ATR of TD+MN(O<sub>2</sub>/C=0.3 and S/C=1.5)

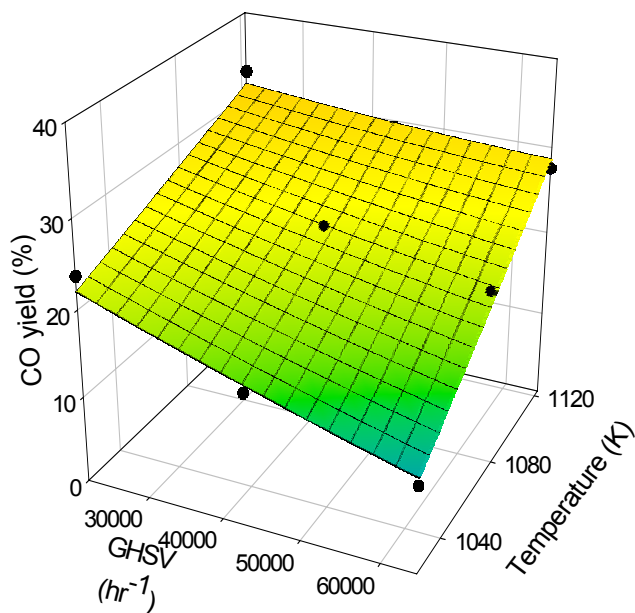


Fig 7. Yield of CO from ATR of TD+MN (O<sub>2</sub>/C=0.3 and S/C=1.5)

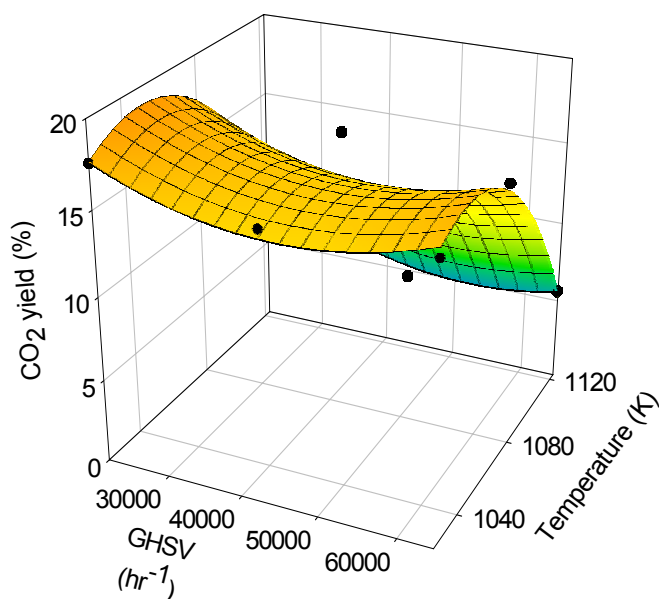


Fig 8. Yield of CO<sub>2</sub> from ATR of TD+MN(O<sub>2</sub>/C=0.3 and S/C=1.5)

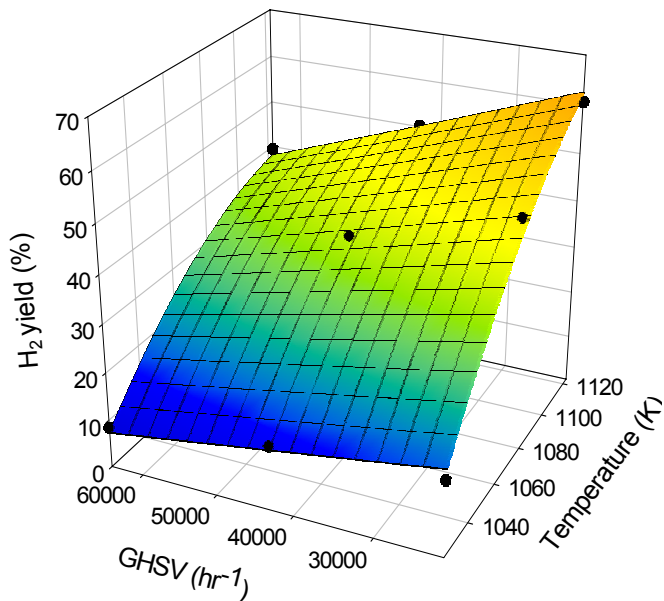


Fig 9. Yield of H<sub>2</sub> from ATR of MN+DHN(O<sub>2</sub>/C=0.3 and S/C=1.5)

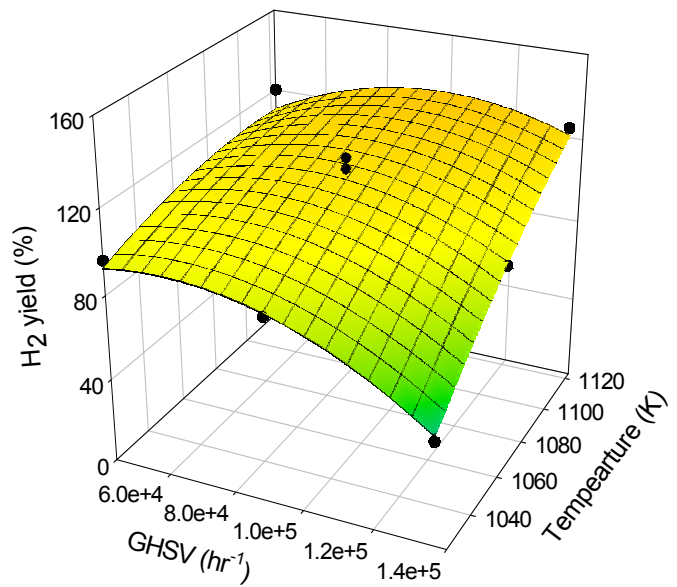


Fig 10. Yield of H<sub>2</sub> from ATR of TD+DHN(O<sub>2</sub>/C=0.3 and S/C=1.5)

Difference in the relative reactivity of components in a binary mixture as well as the type of reforming performed plays important roles in the reforming of a binary mixture representing a diesel fuel to produce syngas. Overall yields from a binary diesel mixture are not simply additive of yields from individual fuel components. Relative reactivity of one fuel component considerably affects the conversion pattern of other as well as the overall product distribution. More the difference in reactivity of binary components, larger the effect on reforming is noticed. For example, aromatics are relatively less reactive compared to paraffins, hence the highly reactive paraffins would consume available O<sub>2</sub> in POX and ATR reactions. Therefore, conversion of highly reactive fuel component proceeds towards the completion and it produces combustion products. While, O<sub>2</sub> is not spared enough for the less reactive component, consequently less reactive component is predominantly subjected to pyrolysis reaction. POX was affected significantly by the difference in the reactivity of fuel components. While, SR was not affected much from the difference in reactivity of fuel components since water was present in abundance in steam reforming. ATR was somewhere in the middle.

Side reactions specific to one component play important role in reforming of a mixture. For example, aromatics are more coking prone upon reforming, therefore its presence in the mixture can lower the yields of syngas over time due to catalyst deactivation. Also, the catalyst surface-component interaction may play important role in the reforming of a mixture. For example, aromatics have abundance of  $\pi$ -electrons so it may occupy catalyst active sites for longer time due to  $\pi$ -complexation between d-orbitals in the metal and  $\pi$ -electrons. Hence, there won't be enough reactive sites available for the desired reaction to occur.

## References

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