COMPARATIVE STUDY OF HYDROCARBON FUEL REFORMING PROCESSES AND PRODUCTION YIELDS OF SYNTHESIS GASES OF H_2, CO_2 AND CO

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Theoretical study was conducted to investigate the distinction between cracking systems process technologies. The purpose is to feed pure hydrogen gas to the fuel cell as the renewable energy power source. Three types fuels of Hydrocarbon were involved namely gasoline, iso-octane and diesel. Theoretical calculations and synthesis gases of hydrogen, carbon dioxide and carbon monoxide were carried on. Steam reforming process of gasoline achieved a conversion of 68%, 75% for iso-octane and 55% for diesel. Auto thermal reforming produced 55% of H_2 for gasoline via 35% for iso-octane and diesel. The process of dry reforming produced 50% of H_2 for gasoline and 35% for iso-octane and diesel. The amounts of CO2 were analyzed for the cracking processes of the same gases. CO_2 generated in steam reforming was 40, 35 for iso-octane and 25% for diesel. Auto thermal reforming amount was 25% of CO_2 for gasoline and 28% for iso-octane and 40% for diesel.   Dry reforming process reached an amount of gas of 35% of gas for steam reforming process of gasoline and 30 for iso-octane and 25% for diesel. Generation of CO gas for gasoline, iso-octane and diesel were also performed. Steam reforming processes contain 30%, 30%, 35%; respectively. Auto thermal cracking produces 30%, 30%, 45% of CO; respectively and in comparison with 35%, 25%, 44% of CO from dry reforming type processes. Data regarding cracking reforming chemical process [1, 2] were evaluated and recognized some disagreement.

KEY WORDS: *Steam reforming; Auto thermal; Dry reforming; Diesel; iso-octane; gasoline.*

INTRODUCTION

Fuel cells are promising technology that can provide heat and electricity as long as fuel (hydrogen) is supplied [3]**.**

Hydrogen possibly withdrawn from hydrocarbons by applying adequate heat necessary to separate the hydrogen form hydrocarbons is due to the fact that it is one of its main ingredients [3]**.**

Small scale chemical plants usually use auto-thermal chemical process since it satisfies and fits the reactor criteria. The fuel cell which is the main part of the alternative power source system demand the use of pure hydrogen; that is the output of

hydrocarbon fuel cracking system with minimum sulfur, as well as natural carbon. By the time that the hydrogen power system sees the light then it would be the source of power that may be adopted by many governments all over the world. Therefore, an efficient chemical process power plants to renovate hydrocarbon fuels to synthesis type gases such as methane and carbon dioxide as well as the main source of power type gas "hydrogen" faces many chemical challenges from the point that the reaction starts to the stage of operation where the power system generates hydrogen. Developing a powerful hydrogen power system technology to crack and renovate hydrocarbon fuel demands that all problems associated to convert fuels to synthesis gases must be resolved to ensure that the catalyst inside the chamber of reaction which in charge of the fuel conversion operational process withstands the effect of temperatures and pressures that may generate within system as result of fuel processing of hydrocarbon fuels. Unlike battery type source of powers, fuel cells use a continual supply of reactants to generate a power that is pollutant free.

The investigations in this work accounts the experimental consequences of chemical conversion conditions for different chemical type processes.

Internal traditional combustion process as means of power with all chemical and environmental problems served as the driving force for many administrations to become accustomed to more decent fuel cell power systems with respect to power efficiency since heavy hydrocarbon power type fuel is available and recommended to be most favorable fuel power systems. Fuel cell provided by a network of both portable and distributed hydrogen power generation is what made the technology to be the best alternative for future power source. The three different chemical catalytic type operations of auto-thermal, steam and dry reforming chemical process are responsible and in charge of renovating hydrocarbon fuels such as gasoline into synthesis gases of hydrogen type. Organic compounds contain Hydrogen make up many of our daily hydrocarbon type fuels (gasoline, methanol, and natural gas) [3]. . Large chemical plants adopt steam reforming chemical systems that utilize the excess heat available from other processes. Reforming of hydrocarbon fuels to generate hydrogen will create a pollution free world for people to live in, by developing an environmentally friendly alternative energy sources.

High temperature is recommended to minimize the effect of water and the outlet gas stream must be well treated before feeding the hydrogen into the fuel cell. The reason that should the effluent gas stream of hydrogen must be pure is that any presence of a few parts per million of bonded or unbounded sulfur could be sufficient to destroy the catalyst. The formation of carbon monoxide and carbon dioxide at a certain level of temperatures must be accounted for to assure that the amount of hydrogen as high as possible and that for carbon monoxide to be as few as it could be and to renovate some of the carbon monoxide to more of a carbon dioxides.

Ahmad *et. al.* developed an auto thermal reforming catalyst process that converts gasoline to hydrogen, carbon monoxide, and carbon dioxide at a temperatures of 550 °C and demonstrated a complete conversion of these feeds, producing enough hydrogen to power a 5-kW fuel cell stack [3].

Due to low ratio of hydrogen to carbon and to the high molecular weight of hydrocarbon fuel type such as diesel fuel, thermal cycling leads to possible thermal shock that assist in soot formation which certainly lead to catalyst deactivation.

Systems of high temperatures improve conversion, resulting in better system efficiency, but reduce material stability [3].

Cracking unit of hydrocarbon fuels is to produce synthesis gases of H_2, CO_2, and CO with feeding hydrocarbon fuel and water directly to the process. Catalysts must withstand heat and survive as much as possible to ensure that optimized parameters are employed to the system. The chemical process that converts hydrocarbon fuels to gases must be able to purify hydrogen and design for boundary conditions of higher efficiency. Hydrocarbon fuels may produce methane, hydrogen, Carbon monoxide as well as carbon dioxide in different quantities. The amount of sulfur and carbon on catalyst must be measured well to enhance reaction rate and exploit then a synthesis gases as possible. Sulfur and carbon agents affect cracking process and must be pretreated before the start up of reaction.

Steam catalytic type reforming process coupled with a separation hydrogen purification technology membrane unit must serve as a complementary power hydrogen generation system afford to reform a variety of hydrocarbon fuels to produce hydrogen and other gases. A hydrogen power system accompanied and equipped with a separation membrane in order to maximize hydrogen percentage must also account for lower quantities of carbon monoxide and carbon dioxide.

EXPERIMENTAL METHODS

Auto-thermal type chemical process functions as an integration unit equipped with dual catalysts. The conversion of hydrocarbon type fuels into combination of gases performed by catalyst attached with membrane unit to purify the hydrogen gas.

The experimental work conducted at 550C° included that the agent of sulfur in reforming process must be removed at the start up of the thermal cycle process by feeding fuel and water to the top of the reaction unit system. Pure oxygen gas is employed to improve the revealing process of any mono-aromatics or di-aromatics constituents related that may be present in the product stream. Effluent stream of synthesis gases produced and analyzed by a chromatograph [4]. The operation provides a homogeneous mixture of water, air, and fuel to be injected into the burner unit system. Heat is essential to accomplish reforming process well and to ensure the reaction continuity by transferring energy to the catalytic reaction chamber passes over pellets of reforming catalysts. Gases of H_2, CO_2, and CO were produced and cleaned before been withdrawn from the operation with respect to H_2 which provides a feed stock to the targeted fuel cell [4].

METHODOLOGY AND CALCULATIONS

The system temperature for cracking the feedstock of hydrocarbon fuels was optimized and set up at 550 °C. Active surface of catalyst is assumed to be varying as a function of excess heat that is the "oxygen: fuel ratio". Dry, nitrogen-free basis is also assumed through carrying on calculations throughout the system.

The preferential reaction of the water-gas shift reaction produces carbon dioxide as well as carbon monoxide:

$$\{(CO + \tfrac{1}{2}O_2 \rightarrow CO_2)$$

Also, the water-gas shift reaction will take place as a secondary reaction:

(CO + H$_2$O ↔ CO$_2$ + H$_2$)}.

The reaction stoichiometry that conducts the hydrocarbon of iso-octane fuel:

Iso − C$_8$H$_{18}$ + 8 H$_2$O → 8 CO + 17 H$_2$ ΔH_r^o = +1275 kJ/ mol of iso-octane
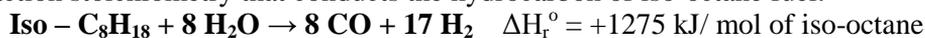
The standard heat of reaction is strongly endothermic.

The undesired reaction that consumes hydrogen:

CO + 3 H$_2$ →   CH$_4$ + H$_2$O ΔH_r^o = -41 kJ/ mol of CO
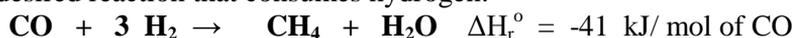
The above chemical reaction is slightly exothermic.

The processing system:

Carbon-fuel based:

Gasoline, iso-octane or diesel, and water to generate hydrogen

Synthesis gases:

Hydrogen (H$_2$), carbon monoxide (CO), and carbon dioxide (CO$_2$)

RESULTS AND DISCUSSIONS

The amount of compounds associated with effluent stream of hydrogen, carbon dioxide and carbon monoxide were evaluated in streams of feed, reject and permeate. The catalyst must be always as active as possible for accurate calculations. Full activity is assumed by the pellets of catalyst inside the reaction chamber and all sites displayed by the surface of the reaction particles are available for all types of reactions, this make the conversion high and continuous during the conversion process. A fully active catalyst is monitored by activity which goes down as more carbon deposits on pellets of catalysts. Analysis of theoretical assumptions and calculations were carried on streams of reformat displayed by tables 1, 2, and 3 of auto thermal, steam , and dry reforming; respectively. The catalytic cracking process cracks the feedstock of hydrocarbon fuel reforming at lower temperatures than other commercial type catalysts**.** A theoretical hydrogen recovery for the three cracking chemical processes of converting hydrocarbon fuels into synthesis gases were found to be 60%, 68%, and 55%; respectively.

To ensure that a high conversion of hydrocarbon fuels into hydrogen, it should be taken into account the calculations of both quantities of carbon dioxide and carbon monoxide. A conversion towards carbon dioxide plays a role in maximizing pure hydrogen and minimizing carbon that may be deposited on catalyst.

Reducing and proposing a reaction that maintains the amount of carbon monoxide as minimum as possible or to manage the mechanism of such a reaction must be established since preferential reaction of carbon monoxide must be employed within the system joining the water-gas shift reaction:

{(CO + ½O$_2$ → CO$_2$) + (CO + H$_2$O ↔ CO$_2$ + H$_2$)}

Available poisoning pellets of catalysts for reactions disturbs and affects the cracking conversion system from the startup of the cracking chemical process due to soot formation which increases as the time do.

The figures below discuss the amount of hydrogen, Carbon dioxide and carbon monoxide reformat achieved in different cracking processes analysis of gasoline.

Figure 1 shows that the steam reforming process for gasoline achieved a conversion that is close to 68%. The high conversion indicates the fact that the

cracking process reached optimum conversion at a higher temperature of 400C while the activity of catalyst survived the reaction soot and carbon deposited.

Table 1: Compound of Reformat Process Analysis of "Gasoline" fuel of Hydrogen

Reformat Compound	Auto thermal	Steam Reforming	Dry Reforming
Feed to the Fuel Cell	55	68	50
Reject	20	20	10
Permeate	100	100	100

Table 2: Compound of Reformat Process Analysis of "Gasoline" fuel of Carbon Dioxide

Reformat Compound	Auto thermal	Steam Reforming	Dry Reforming
Feed to the Fuel Cell	45	40	20
Reject	35	35	30
Permeate	0.0	0.0	0.0

Table 3: Compound of Reformat Process Analysis of "Gasoline" fuel of Carbon monoxide

Reformat Compound	Auto thermal	Steam Reforming	Dry Reforming
Feed to the Fuel Cell	30	20	35
Reject	45	25	25
Permeate	0.0	0.0	0.0

Table 4: Compound of Reformat Process Analysis of "iso-octane" fuel of Hydrogen

Reformat Compound	Auto thermal	Steam Reforming	Dry Reforming
Feed to the Fuel Cell	35	75	35
Reject	20	30	25
Permeate	100	100	100

Table 5: Compound of Reformat Process Analysis of "iso-octane" fuel of Carbon Dioxide

Reformat Compound	Auto thermal	Steam Reforming	Dry Reforming
Feed to the Fuel Cell	28	35	30
Reject	36	35	28
Permeate	0.0	0.0	0.0

Table 6: Compound of Reformat Process Analysis of "iso-octane" fuel of Carbon monoxide

Reformat Compound	Auto thermal	Steam Reforming	Dry Reforming
Feed to the Fuel Cell	30	30	25
Reject	42	44	35
Permeate	0.0	0.0	0.0

Table 7: Compound of Reformat Process Analysis of "Diesel" fuel of Hydrogen

Reformat Compound	Auto thermal	Steam Reforming	Dry Reforming
Feed to the Fuel Cell	35	55	35
Reject	20	25	15
Permeate	100	100	100

Table 8: Compound of Reformat Process Analysis of "Diesel" fuel of Carbon Dioxide

Reformat Compound	Auto thermal	Steam Reforming	Dry Reforming
Feed to the Fuel Cell	40	75	35
Reject	45	40	40
Permeate	0.0	0.0	0.0

Table 9: Compound of Reformat Process Analysis of "Diesel" fuel of Carbon monoxide

Reformat Compound	Auto thermal	Steam Reforming	Dry Reforming
Feed to the Fuel Cell	45	35	40
Reject	42	22	30
Permeate	0.0	0.0	0.0

Dry reforming process apparently behaved steadily with suspect to conversion and seems that it suffers from carbon deposited on the surface of catalysts which is no longer available for reaction. The activity of pellets of catalysts seems to affect the conversing rate and pearly reached 28%.

The process of auto thermal reforming did seem to suffer from catalyst poisoning right at the beginning of the reaction. The conversion rate was even lower than that provided by the dry reforming process. As it could be seen from the rate of the reaction, there is somehow a source of catalyst regeneration taking place towards the end of the reaction. The conversion rate reached 25% and at the end of the reaction the catalyst seemed to had enough temperature exhausted and yet most of the pellets were out of order with respect to reaction rate and activity.

Figures 1, 2, and 3 show the amount of H_2 in different chemical processes notified by: ● = Steam Reforming; × = Dry reforming; ▲ = Auto thermal reforming

Figure 2 shows the fact imposed by the steam reforming process for converting most of the hydrocarbon fuel of gasoline to hydrogen gas. For some reason the amount of conversion achieved were more for iso-octane than gasoline which in fact reached over 75%. The conversion indeed is over whelming which reflects that the cracking process during the operation of high temperature system withstand the soot and carbon continuous formation during the course of reaction.

The chemical cracking process of dry reforming apparently reached the 35% and cooked fast to the point that the conversion lowered as the reactants spend more time passing over the catalyst.

In auto thermal cracking process, poisoning affected the catalyst at the start up of the reaction and start building up in a consistent manner. The conversion rate according

to this process got to be around 35% and withstand the temperature effect for over 65 hours. In figure 3, the fact here is some how different than gasoline and iso-octane.
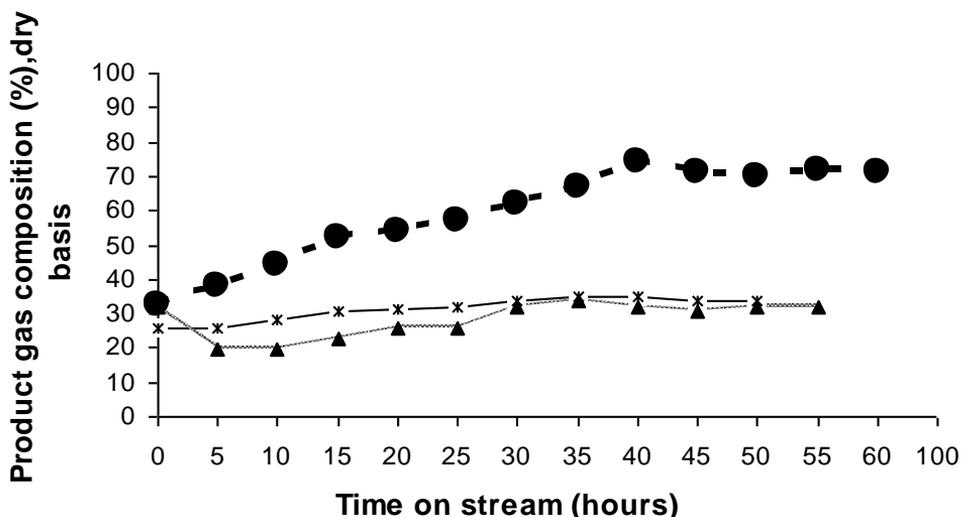
Figure 1: H_2 reformat in process analysis of Gasoline
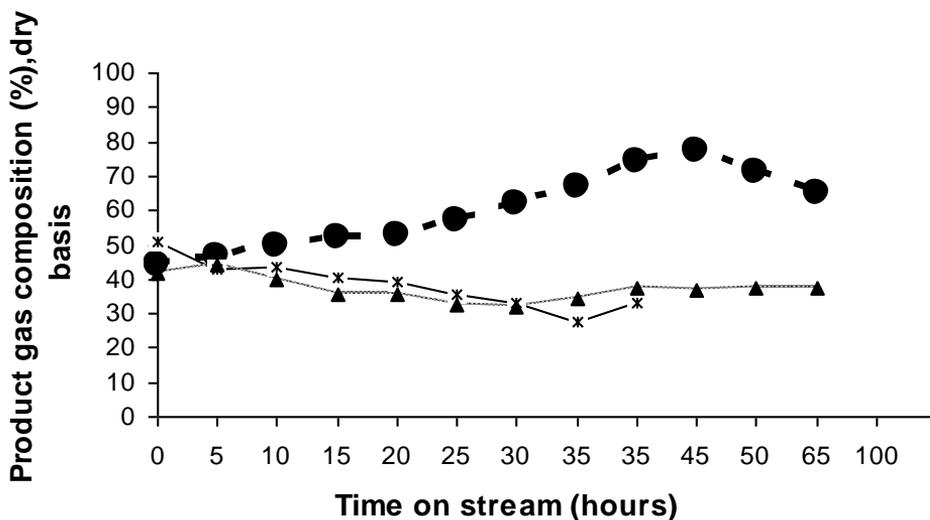
Figure 2: H_2 reformat in process analysis of Iso-octane.

The conversion rate for diesel was lower than gasoline and iso-octane. The catalyst involved only survived 45 hours which is considered to be low when compared with to other types of fuels.

The process of cracking heavy hydrocarbon type fuels must deal with more drawbacks and soot formation with respect to conversion which is the factor that most of the time provides the success of such operation.
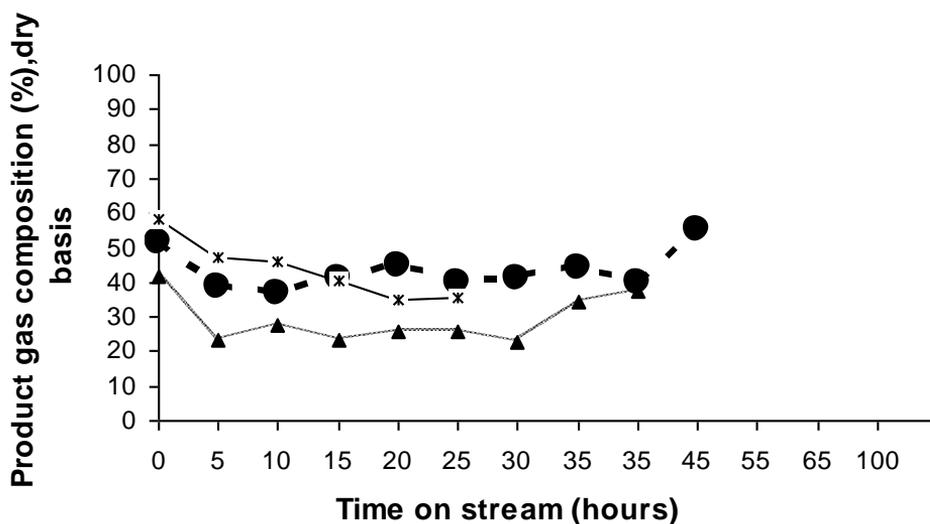
Figure 3: H_2 reformat in process analysis of Diesel.

Figures 4, 5, and 6 show the amount of CO_2 in different chemical processes notified by: ● = Steam Reforming; × = Dry reforming; ▲ = Auto thermal reforming

The reformation process carried on survives only for 65 hours, whereas that for dry reforming withstand only for 20 hours. Cracking such type of fuel as seen by the above figure seems to deal with more carbon formation at the start up of the reaction than any other fuels. The conversion reached around 55% by the steam reforming process, whereas did not reach 35% by other cracking processes.

In the above figure, the steam reforming processes seem to have more carbon dioxide than any other cracking processes producing almost the same amount of gas for over 30 hrs in constant manner and stayed in the reactor for more than 65 hrs as well.

The dry reforming process of gasoline type fuel got to have around 30% of carbon dioxide and survived the reaction up to 20 hours. Whereas the auto thermal cracking process survived almost 55 hours and contained only 25% of CO_2.

The cracking method that took place carried on by hydrocarbon fuels of iso-octane suffered more of a carbon monoxide formation and a certain amount of carbon dioxide as well. The driving force for accomplishing better results is to establish a reaction to convert more of CO to CO_2. The disproportion phenomenon of CO_2 generates a bad carbon cursor that causes a direct effect and must be accounted to in all theoretical calculated amounts of H_2.

In figure 5 the steam reforming processes has been survived for 20 hours for iso-octane and contains 35% of carbon dioxide. The dry reforming process contained 25% and withstands about 35 hours.

The auto thermal reforming process of iso-octane type fuel contained around 20% of carbon dioxide and survived 20 hours.
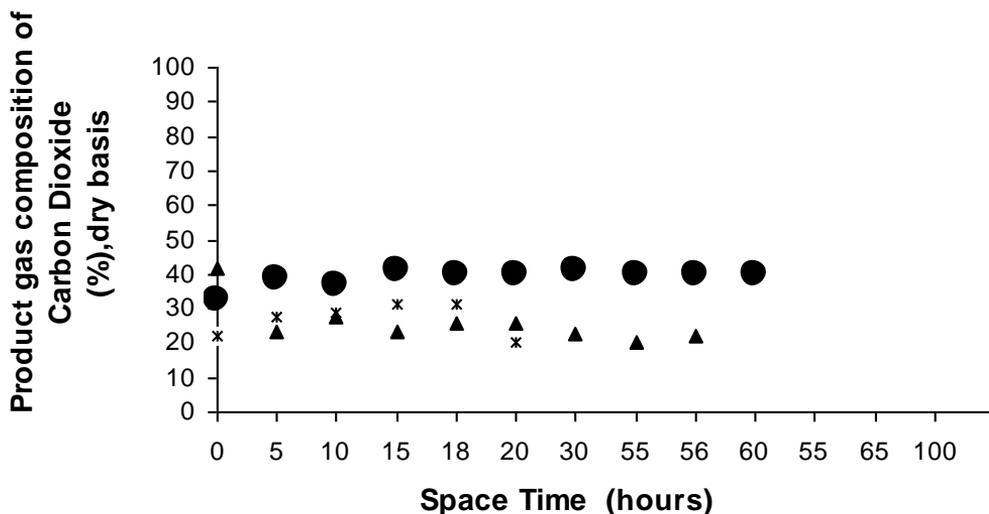
Figure 4: CO_2 reformat in process analysis of Gasoline.
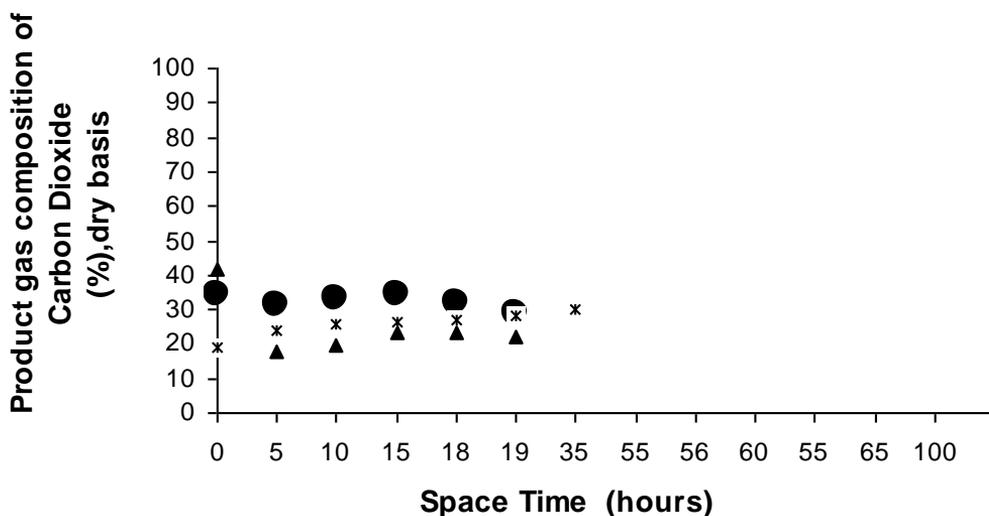
Figure 5: CO_2 reformat in process analysis of Iso-octane.

In figure 6 the steam reforming processes seem to have better results one more time than any other processes (dry or auto thermal). The steam reforming process survived 55 hours whereas the dry reforming survived heat and soot for only 35 hours. The amount of carbon monoxide was around 40% for the steam reforming process and less than 25% in other processes.

Figures 7, 8, and 9 show the amount of CO in different chemical processes notified by: ● = Steam Reforming; × = Dry reforming; ▲ = Auto thermal reforming

Figure 7 shows the quantity of carbon monoxide formation of the three cracking reforming processes involved in this study. Steam reforming provides a smaller amount

of CO than other cracking processes. The few amount of CO provided by the system indicates that most of the carbon is either migrated the CO to the atomic site of CO_2 or converted through a reaction called disproportion reaction where not all carbons would be able to be deposited on the surface of the catalyst inside the chamber of the reactive unit.
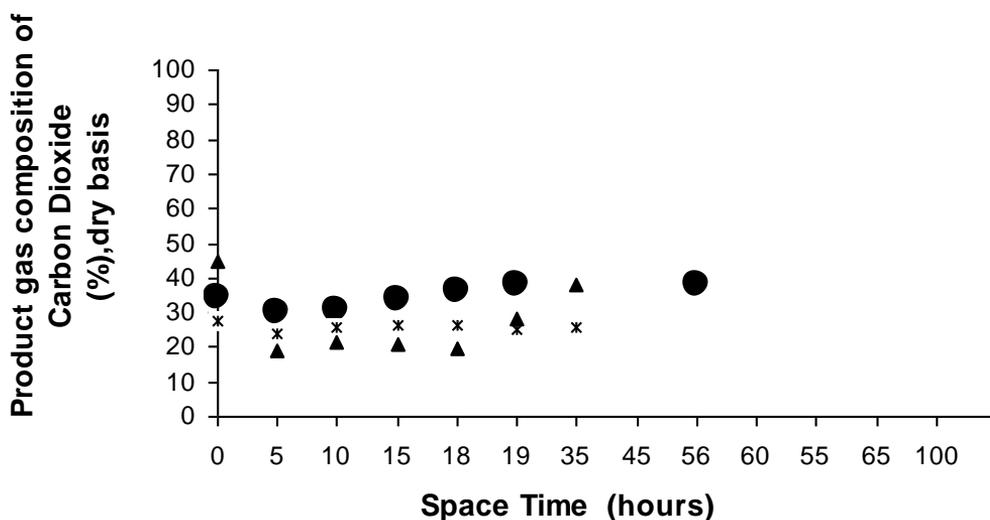
Figure 6: CO_2 reformat in process analysis of Diesel.
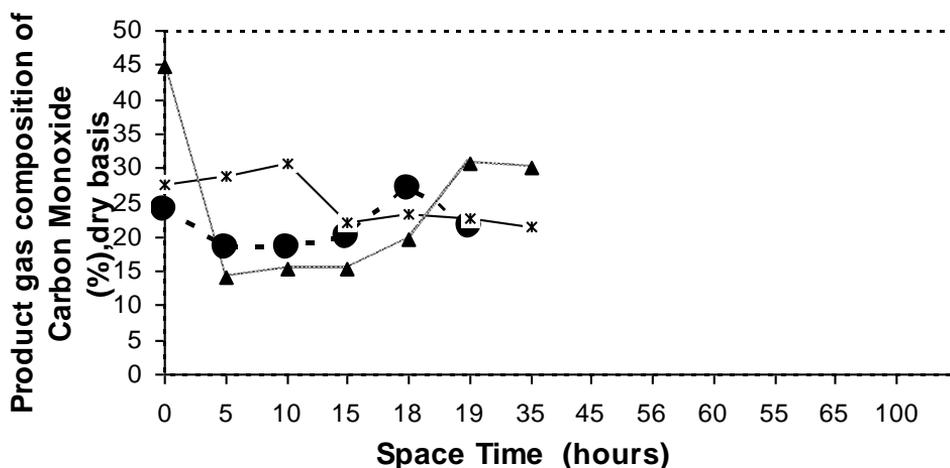
Figure 7: CO reformat in process analysis of Gasoline.

Figure 8 proved that the amount of CO evolved seem to be more this time with steam reforming than dry or auto thermal cracking processes. There is a sort of regeneration reaction that need to be further studied going through the auto thermal reforming that we did not experience another processes.
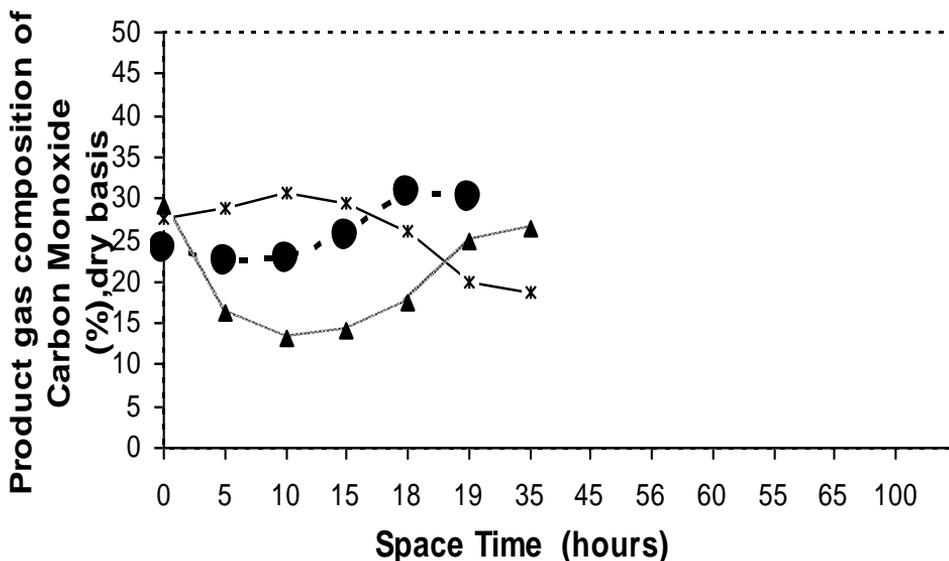
Figure 8: CO reformat in process analysis of Iso-octane.

Figure 9 shows that the amount of CO that evolved by the cracking process system in steam reforming is less than that in auto thermal cracking. The reaction that converts carbon monoxide to carbon dioxide seems to be more feasible in auto thermal processes than steam reforming or dry reformation unit system.
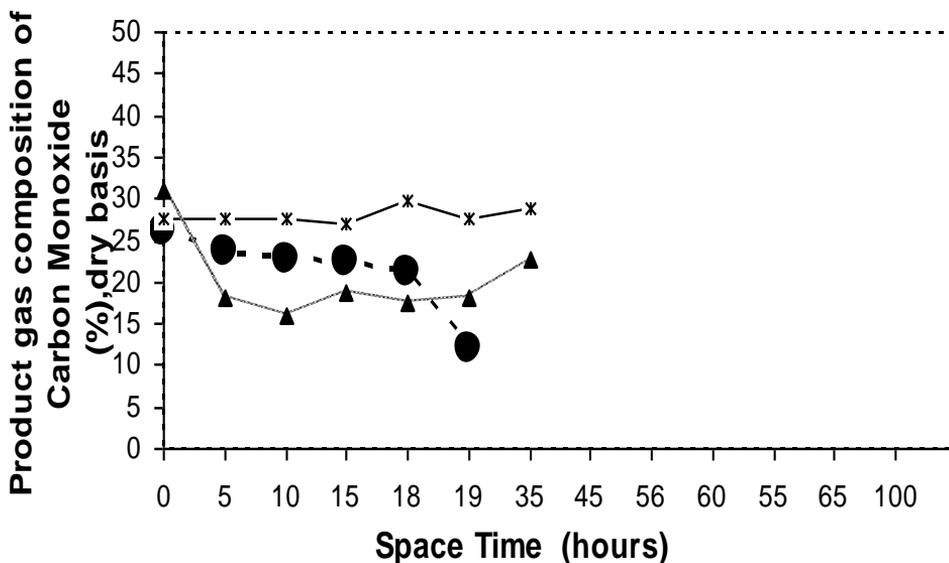
Figure 9: CO reformat in process analysis of Diesel.

CONCLUSION

The study is conducted to observe the difference between the three cracking systems technology. The purpose of the study is however to be able to feed pure hydrogen gas to the fuel cell unit operation. The study tested three different types of hydrocarbon fuels that contain different chains of stiff carbons which may affect the soot phenomenon.

Hydrocarbon type fuels involved in the study are gasoline, iso-octane and diesel type fuels. In all cases the theoretical analytical calculations involved the amount of synthesis gases of hydrogen; carbon dioxide and carbon monoxide were taken into account in order to come up with a sort of reaction to maximize the amount of hydrogen gas. Also the amount of both synthesis gases of CO and CO_2 play a role since we are yet looking for a methodology to increase the conversion of CO to CO_2. However; among all the three cracking chemical processes the best one of reformatting hydrocarbon fuels to synthesis gases is the steam reforming process. For all the studied fuels, the production of H_2 is higher and the amount of CO is lower. The catalyst also is the driving force for good conversion which reflects the fact that there is a possibility to stay longer in the reaction bed where more conversion expected. Diesel fuel remains the challenges for its stiffness to extract as much hydrogen as possible and with little carbon monoxide to ensure that the system is capable to withstand high temperature elevation as well as pressure imposed by other factors in the reaction chamber.

FUTURE WORK

We recommend to evaluate different types of catalyst and to evaluate their influence at different process conditions. Temperatures must be one of the parameters that the investigation may include as well as the water to carbon ratio.

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مقارنة بين أنواع الوفود الهيدروكربونية و إنتاج غازات الهيدروجين وثاني أكسيد الكربون وأول أكسيد الكربون

تم إجراء هذه الدراسة بغرض التمييز بين مفاعلات إنتاج غازات 2CO2 , CO, H من ثلاثة أنواع من الوقود هي (الجازولين – والايزو اوكتان والديزل) مع استخدام عدد من المحفزات الكيميائية (Molybdenum Carbide, Tungsten Carbide & Zinc Oxide).

وتم استخدام ثلاثة طرق للمعاملات الكيميائية للحصول على الهيدروجين ؛ هي التحويل بالبخار والتحويل الجاف والتحويل ذاتي الحرارة. وقد تبين من الدراسة أن التحويل بالبخار هي أفضل طريقة لإنتاج اكبر كميه من الهيدروجين.

أما من الناحية التطبيقية والاقتصادية يمكن أن تؤدي نتائج هذه الدراسة إلى أن إنتاج غاز الهيدروجين من أنواع الوقود المختلفة وخاصة الديزل يستخدم في خلايا الوقود .