

An Experimental Study on Methane and Gasoline Reforming for Hydrogen Rich Gas Generation Using Non-Thermal Microwave Plasma

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ABSTRACT: There are many different types of hydrogen forming technologies and subsequent application of hydrogen generated from this process. The main purpose of this study is to investigate the performance of a newly developed low-cost microwave plasma system and its applicability for hydrogen generation. SCR (Selective Catalytic Reduction) could be a potential application for hydrogen generated by plasma systems or catalyst-assisted plasma systems. In this study, both methane and gasoline were reformed to generate hydrogen rich gas using a non-thermal microwave plasma reactor and the fundamental aspects of fuel reforming performance was evaluated. The experimental results show that the elevation of applied input power and the decrease of the total flow rate led to the increase of hydrogen and carbon monoxide yields. In case of methane reforming, when the feeding concentration of methane was about 1% of the total flow rate and O/C ratio was between 1.1 and 1.4, maximum hydrogen and carbon monoxide yields were achieved. As for the gasoline, the maximum syngas (H_2+CO) yield was observed when O/C ratio was 1.1.

Keywords: Hydrogen, Reforming, Non-thermal plasma, Methane, Gasoline

1. INTRODUCTION

Hydrogen is currently being widely used both as a raw chemical and a gas ingredient. Furthermore, it is regarded as a promising alternative energy resource or an energy carrier, if we take into account the price of environmental issues and fossil fuel depletion facing humanity. Also, Hydrogen has a wide range of applications such as

exothermic combustion systems, fuel cells, and in automotive exhaust gas reduction devices. Thus, hydrogen has a strong potential to be the cornerstone of a new energy infrastructure in the future.

Our ultimate goal is to obtain hydrogen from renewable energy resources, but for the short term, getting hydrogen from fossil fuels has many advantages in the sense that it is economical and contributes to the clean

use of hydrocarbon fuels with respect to fundamentally reducing carbon dioxide (CO_2) without drastic changes to conventional combustion systems.

A variety of hydrogen production processes from hydrocarbon fuels are available. These include steaming reforming [1,2], partial oxidation reforming [3], CO_2 reforming[4], thermal plasma reforming [5,6] and others.

Among them, steam reforming is widely used because of advantages such as gas throughput and hydrogen yield, but it has disadvantages of large reactor size and slow reaction speed. Moreover it needs high temperature and high pressure due to its intrinsic characteristic of strong endothermic reactions. Also if we use the catalyst to raise the hydrogen yield in steam reforming, it is likely to degrade the performance of the catalyst due to the substances such as sulphur.

Thermal plasma reforming that can accelerate chemical reactions as the result of high-temperature effects has the advantage of rapid start-up and responsibility and free of many shortcomings (i.e., high pressure etc.) of steam reforming. However, it also has a problem in that high electrical energy is required to keep the high temperatures in the plasma discharge.

Therefore, hydrocarbon reforming using non-thermal plasma is an effective way to solve these disadvantages.[7] Non-thermal plasma reforming is a high-efficiency process because a non-thermal plasma is cold relative to thermal plasma, so therefore requires less energy input to sustain the discharge.

The main purpose of this study is to investigate the performance of a newly developed low-cost microwave plasma system and its applicability to hydrogen generation. Especially, we are targeting the possibilities of an on-board hydrogen generation system that can be applied to fuel cells and HC-SCR (Hydrocarbon-Selective Catalytic Reduction). The SCR is the one of the promising technologies with which to

reduce NO_x emission from the automobile exhaust gas.

HC-SCR uses hydrocarbons as a reductant. When compared to other SCR systems such as Urea-SCR, its performance to reduce NO_x is relatively low. However, many researches show that adding hydrogen to HC-SCR system can improve its performance.[8,9]

For these reasons, it is an important research topic to study on-board hydrogen generation from hydrocarbon fuels using non-thermal plasma reformation.

In this article, various hydrocarbon fuels (methane, iso-octane, gasoline) have been reformed using a non-thermal microwave plasma according to regular plasma input power, concentration of methane (or fuel injected), total flow rate and O/C ratio. Then we have measured the synthetic gas ($\text{H}_2 + \text{CO}$) amount and from these data we have found optimal conditions for plasma reforming.

2. Experimental set-up

2.1 Methane Reforming

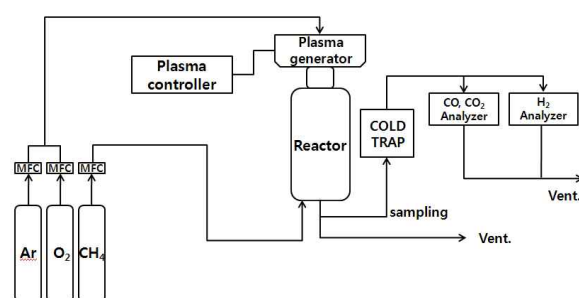


Figure 1: Methane reforming system

Figure 1 shows the schematic of a methane reforming system. Argon (Ar) is used as an inert gas. Flow rates of argon (Ar), methane (CH_4) and oxygen (O_2) are controlled by the mass flow rate controllers (MFC) to enable partial oxidation of methane.

The plasma generator uses argon and oxygen as the base gas for the discharge. The applied input power and ignition power can be separately controlled in the plasma

controller, and we can measure the power consumption by connecting power meter to the plasma controller.

Methane flows through the gas tube installed from the bottom of the reactor to the nozzle of the plasma generator for partial oxidation.(Figure 2) The reason not to put methane into the plasma generator with argon and oxygen at once is to prevent the nozzle choking which can be caused by carbon(C) generation from the plasma reforming.

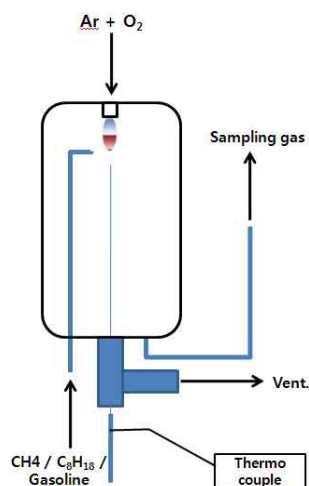


Figure 2: Methane reforming reactor

Before and after experiment, we measure the temperature change by using a thermocouple in the reactor.

A part of reforming products flows through the sampling line to the hydrogen analyzer and the CO/CO₂ analyzer. At this time the sampling gas passes through the gas cooler to remove water particles and then enters the analyzers for an analysis of the product gas.

Plasma reforming conditions are as follows.

Table 1:Experimental conditions for methane reforming

Experiment	input power	concentration of methane
Input power	60~100W	1%
Concentration of methane	80W	0.5~2.0%
Total flow rate	80W	1%

O/C ratio	80W	2%	
Experiment	total flow rate	O/C ratio	reaction time
Input power	7LPM	1	120sec
Concentration of methane	7LPM	1	120sec
Total flow rate	7~12LPM	1	120sec
O/C ratio	7LPM	0.5~2.6	120sec

2.2 Iso-octane & Gasoline Reforming

The Liquid fuels reforming system is based on the methane reforming system. The only change from the methane reforming system is that an evaporation device is added beneath the reactor.

Liquid fuel is injected from syringe at fixed flow rate and passes through a tube which is heated by a heating tape. During this transport process, the liquid fuel is evaporated.

Argon of 0.2 (LPM) is injected to the evaporation device. With 0.2 (LPM) of argon, evaporated fuel can be transferred to the nozzle area of the plasma generator.

Experimental conditions are as follows.

Table 2:Experimental conditions for liquid fuels reforming

Experiment	input power	fuel injected
Input power	60~100W	0.073ml/min
Fuel injected	80W	0.05~0.20ml/min
Total flow rate	80W	0.073ml/min
O/C ratio	80W	0.073ml/min

Experiment	total flow rate	O/C ratio	reaction time
Input power	7LPM	1	120sec
Concentration of methane	7LPM	1	120sec
Total flow rate	7~12LPM	1	120sec
O/C ratio	7LPM	0.5~2.6	120sec

3. Results and Data Analysis

3.1 Methane Reforming

Through these experiments, the following results are obtained.

(1) Plasma reforming according to applied input power

Figure 3 implies that more power input to the plasma causes more production of hydrogen and carbon monoxide and higher temperature change. In addition, power consumption is increased with increasing power input. This result shows that plasma reforming of methane is not conducted completely in low input power.

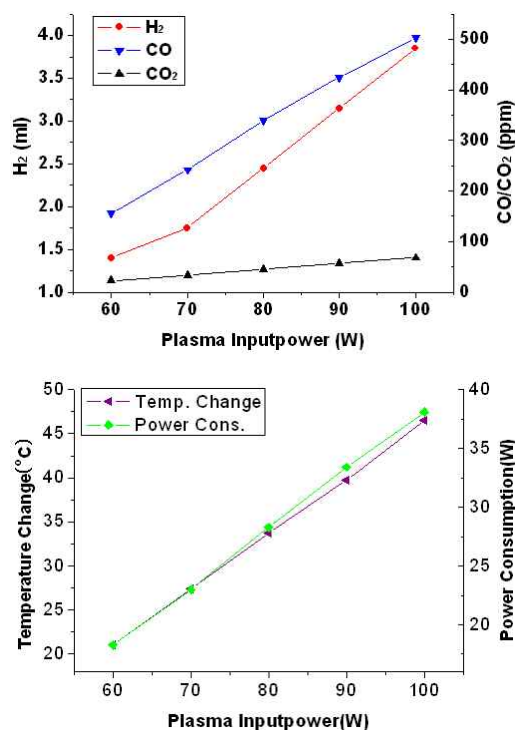


Figure 3: Production of H₂, CO, CO₂ according to power input to plasma / Temperature change in the reactor and power consumption

(2) Plasma reforming according to concentration of methane

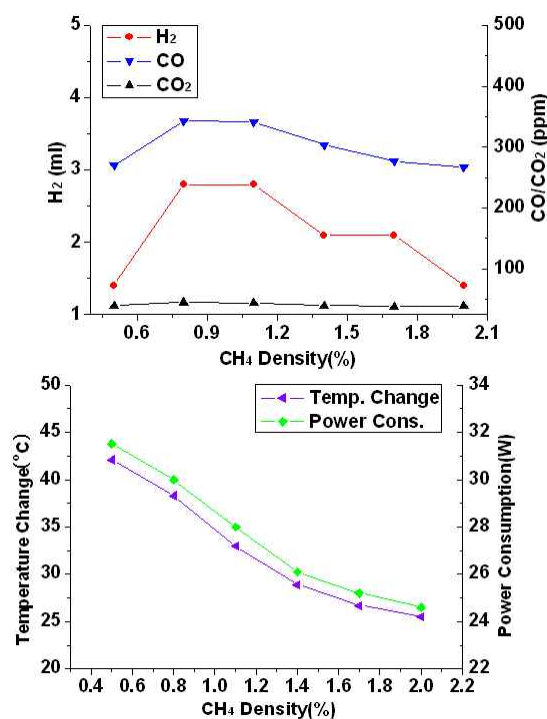
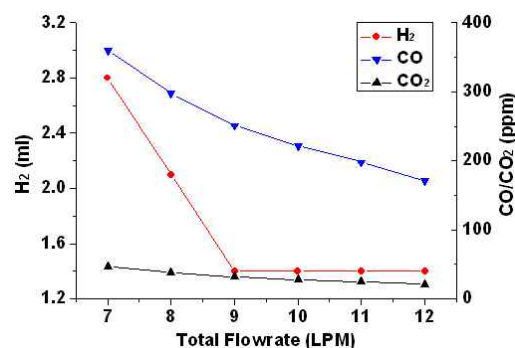


Figure 4: Production of H₂, CO, CO₂ according to methane concentration/ Temperature change in the reactor and power consumption

It is verified through Figure 4 that production of hydrogen and carbon monoxide is at a peak when methane concentration is 0.8~1.1 %. It is also verified that temperature change and power consumption tend to decrease with increasing concentration.

Active reforming reaction is not observed at high methane concentrations. This might be caused by the non-thermal plasma device which has the limited ability for the plasma generation.

(3) Plasma reforming according to total flow rate



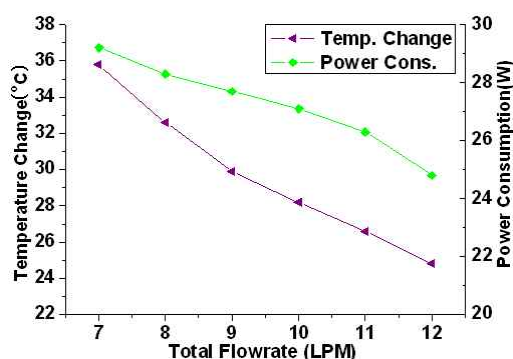


Figure 5: Production of H_2 , CO , CO_2 according to total flow rate/ Temperature change in the reactor and power consumption

Figure 5 shows that increased total flow rate reduces the production of hydrogen and carbon monoxide. Temperature change in the reactor and power consumption tend to decrease with increasing total flow rate. This result shows that the reaction time is not enough to reform the fuel as the total flow rate is increased.

(4) Plasma reforming according to O/C ratio

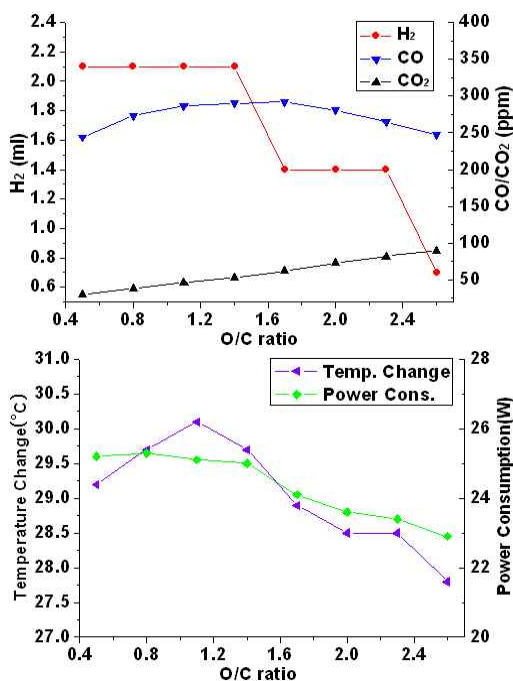


Figure 6: Production of H_2 , CO , CO_2 according to O/C ratio / Temperature change in the reactor and power consumption

It is shown that production of hydrogen and carbon monoxide is maximized at a specific O/C ratio of 1.4.

Figure 6 also shows that CO production is increased for a while but decreased after O/C ratio passes 1.7. CO_2 production, however, is increased continuously, because CO_2 production reaction becomes more dominant with abundant oxygen.

3.2 Iso-octane & Gasoline Reforming

(1) Plasma reforming according to applied input power

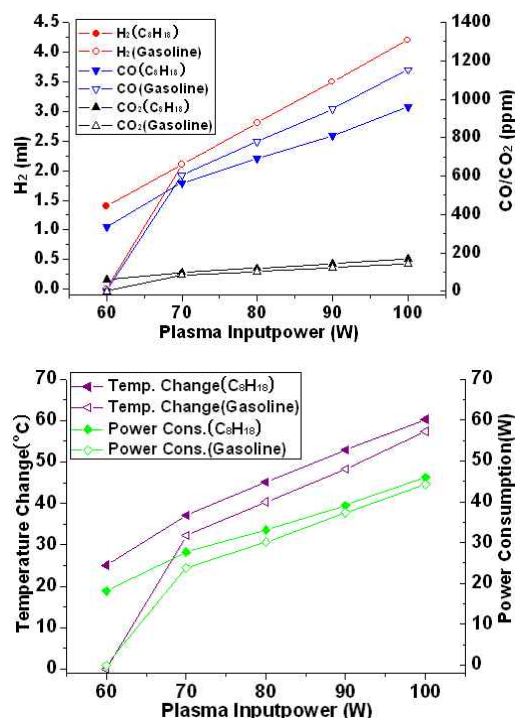


Figure 7: Production of H_2 , CO , CO_2 according to input power to plasma / Temperature change in the reactor and power consumption

It is hard to generate stable plasma when power input is 60 W and the fuel is gasoline. This is not observed for iso-octane.

The difference in hydrocarbon components between gasoline and iso-octane might be the reason for this phenomenon. Unlike iso-octane, gasoline consists of diverse hydrocarbons.

Like methane reforming experiments, Figure 7 shows more power input increases

production of hydrogen and carbon monoxide.

Hydrogen production has a similar tendency as methane but carbon monoxide production is more than 2 times that of the methane case.

(2) Plasma reforming according to fuel injected

Peak production of hydrogen and carbon monoxide is observed at 0.15 ~ 0.20 ml/min as shown in Figure 8. This is because of the characteristics of the non-thermal plasma device which has the limited performance.

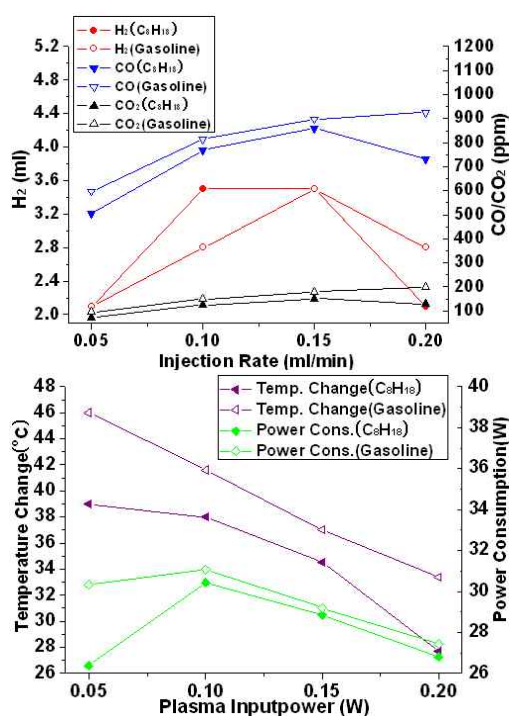


Figure 8: Production of H₂, CO, CO₂ according to fuel injected / Temperature change in the reactor and power consumption

(3) Plasma reforming according to total flow rate

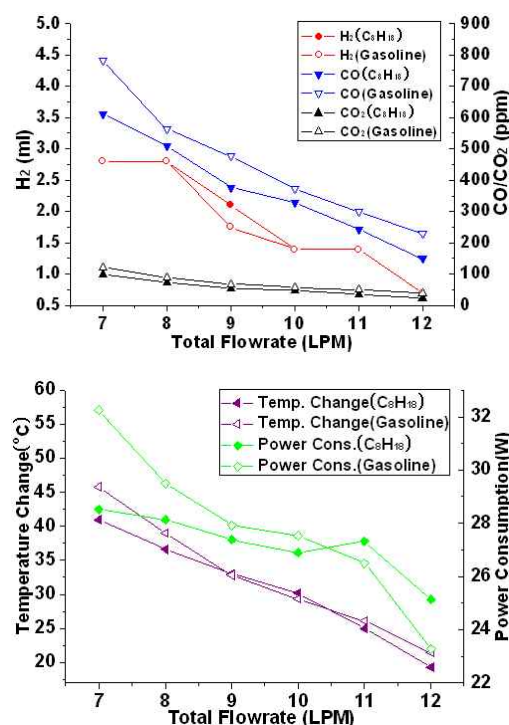
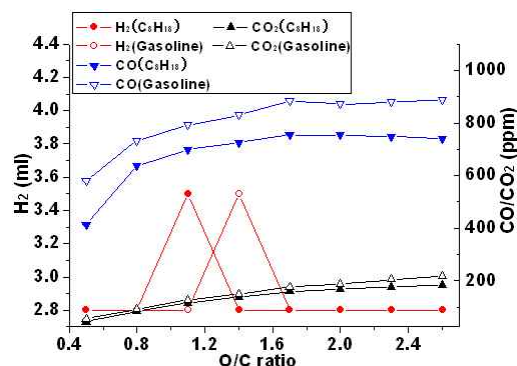


Figure 9: Production of H₂, CO, CO₂ according to total flowrate / Temperature change in the reactor and power consumption

Like the case of methane reforming, more total flow rate makes less hydrogen and carbon monoxide. Temperature in the reactor and real power consumption also tend to decrease. This is because more total flow rate causes shorter residence times of mixed gas in the reactor so the time to react is decreased.

(4) Plasma reforming according to O/C ratio



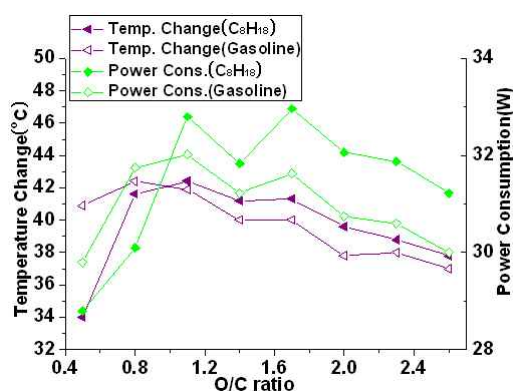
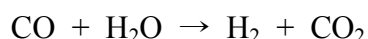


Figure 10: Production of H₂, CO, CO₂ according to O/C ratio / Temperature change in the reactor and power consumption

Figure 10 shows that hydrogen production is at peak when O/C ratio is changed from 1.1 to 1.4. Increasing rate of carbon monoxide production tends to decrease after O/C ratio of 1. Real power consumption is also peaked during in the range of O/C ratio that makes hydrogen production highest.

3.3 Optimal experimental conditions

All of produced carbon monoxide can be assumed to follow the following reaction when transformed into hydrogen.



Optimal conditions considering this fact are as follows.

Table 3: Optimal conditions for reforming

Fuels	concentration of methane (liquid fuels injected)	O/C ratio
Methane	0.8~1.1 %	1.1~1.4
Iso-octane	0.15 ml/min	1.4
Gasoline	0.15 ml/min	1.1

- Plasma Input power : 100 W

- Total Flow rate : 7 LPM

Following result is obtained from conducting experiment under optimal condition.

Table 4: Experimental results for optimal plasma reforming

Fuels	H ₂ (ml)	CO(ml)
Methane	4.2	3.892
Iso-octane	4.2	6.867
Gasoline	4.2	8.561

3.4 Data Analysis

Yield, efficiency and specific energy requirement are calculated based on results from experiments under optimal conditions.

(1) Yield

Yield is calculated by following equation.

$$\text{yield}(\text{H}_2) = \frac{\text{Amount of H atoms in the formed H}_2}{\text{Total amount of H atoms injected}}$$

$$\text{yield}(\text{CO}) = \frac{\text{Amount of C atoms in the formed CO}}{\text{Total amount of C atoms injected}}$$

Yield of hydrogen and carbon monoxide calculated by above equation is following.

Table 5: Yields of H₂ and CO

Fuels	Yield(H ₂)	Yield(CO)
Methane	3	5.56
Iso-octane	4.71	8.67
Gasoline	4.71	10.81

(2) Efficiency (η)

Hydrocarbon reacts with oxygen to produce hydrogen, whose heating value is higher than any other hydrocarbon. Therefore, the efficiency of a reforming system is the lower heating value (LHV) of hydrogen produced divided by the input energy, that is the summation of the electrical energy of the plasma and the LHV of the hydrocarbon injected:

$$\eta = \frac{(\text{H}_2 + \text{CO})_{\text{produced}} \times \text{LHV}(\text{H}_2)}{\text{Input plasma energy} + \text{fuel injected} \times \text{LHV}(\text{fuel})}$$

Table 6: Efficiency

Fuels	Efficiency(%)
Methane	1.28
Iso-octane	1.19
Gasoline	1.36

(3) Specific energy requirement (ν)

This value is the input electrical power used by the plasma that is required for producing one mol of H₂.

$$\nu = \frac{\text{Input plasma power}}{[\text{H}_2 + \text{CO}]_{\text{produced}}}$$

Table 7: Specific energy requirement

Fuels	ν (KJ/mol)
Methane	10829
Iso-octane	9193
Gasoline	7688

4. Conclusion

In this study, methane and liquid hydrocarbon fuels were reformed to generate hydrogen rich gas using non-thermal microwave plasma reactor and the fundamental aspects of fuel reforming performance was evaluated.

1) The elevation of applied input power and the decrease of total flow rate led to the increase of hydrogen and carbon monoxide yields.

2) In case of methane reforming, when feeding concentration of methane was about 1% of total flow rate and O/C ratio was between 1.1 and 1.4, the maximum hydrogen and carbon monoxide yields were achieved.

3) As for the liquid hydrocarbon fuels, the maximum syngas (H₂+CO) yield was observed when O/C ratio was 1.4 (iso-octane) and 1.1(gasoline) and fuel injected was 0.15 (ml/min).

ACKNOWLEDGEMENT

This study was supported by research funds from Korea research foundation and

Specialized graduate school of H₂-fuel cell in Yonsei university.

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