# **CP302: Capstone Project**

# Hydrogen production from Human Urine



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## **Abstract**

The highest energy consumption in conventional centralized wastewater treatment facilities typically arises from the removal of nitrogen compounds through biological processes. An alternative approach involves segregated wastewater systems, wherein wastewater is treated at its source, offering an opportunity to extract value from nitrogen-rich compounds, such as urea. This report explores the feasibility of an innovative method for harnessing energy from human urine, focusing on the isolation of urea before reducing the energy requirements for its thermal decomposition. This approach differs from conventional methods where urea remains in solution. The process begins with the separation of urea from the aqueous solution through adsorption onto activated carbon. Subsequent thermal urea desorption and decomposition at 250°C yield ammonia and CO<sub>2</sub>, effectively regenerating the carbon and maintaining a consistent adsorption capacity. To further enhance the process, coupling the regeneration and urea decomposition step with an ammonia decomposition catalyst result in the production of hydrogen, which can be utilized as an energy source.

# **Contents**

1	Int	troduction	4
2	Ma	aterials	5
	2.1	Activated Carbon	5
	2.2	Ruthenium (Ru) as a Catalyst for Ammonia Decomposition	5
3	Mo	ethodology	6
	3.1	Step 1. Adsorption of urea from domestic wastewater	7
	3.1	.1 Different Isotherm Equations	7
	3.2	Step 2. Desorption and decomposition of urea	8
	3.3	Step 3. Catalytic decomposition of ammonia into hydrogen	9
	3.3	3.1 Equilibrium Decomposition curve of Ammonia	10
4	Co	onclusion	11
5	Fu	ture Work	12
6	Re	ferences	12

### 1 Introduction

Global development depends on having access to energy and water, yet these resources are becoming increasingly scarce due to rising global population and resource-intensive industries. One must create sustainable methods that consume less energy to guarantee that everyone has access to these essential resources, particularly in wastewater treatment plants (WWTPs). By treating wastewater directly at its source, segregated wastewater systems provide a novel method that enables more effective treatment and resource recovery.

An average human being produces 500 L of urine with the amount of urea of 10 kg. As urea has a high content of hydrogen(6.7 wt%) and up to 0.4 kg can be recover from it per person annually. Production of hydrogen is effective as it has a low carbon footprint that is it does not emit carbon during combustion. Hydrogen can be use as a fuel because it has a high energy density.

The three key steps for energy recovery from urine are:

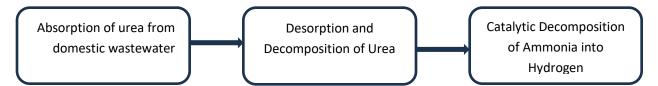


FIGURE 1: STEPS TO RECOVER HYDROGEN FROM UREA IN HUMAN URINE

- 1. **Urea Recovery:** Urea is extracted from the solution using adsorption onto commercial activated carbon within the temperature range of 30°C to 60°C.
- 2. **Thermal Treatment:** The adsorbent is regenerated through thermal treatment, concurrently decomposing urea into ammonia and carbon dioxide at the temperature range of 130 200 °C.
- 3. **Hydrogen Production:** The catalytic decomposition of ammonia is carried out at temperature range of 350-400°C which yields hydrogen and nitrogen.

This method is more environmentally friendly because it requires substantially less energy than traditional treatments. As traditional method is very energy intensive, high temperature requirement for urea hydrolysis which can damage the equipment and low hydrogen yield due to side reaction. By transforming nitrogen-based pollution into useful resources, it also promotes hydrogen as an energy source while lowering energy consumption in WWTPs.

### 2 Materials

#### 2.1 Activated Carbon

Activated carbon is an invaluable material employed for the adsorption of urea from human urine due to its exceptional properties. First and foremost, activated carbon possesses a highly porous structure, characterized by a vast network of irregular pores within a graphitic crystalline matrix. This intricate pore structure offers an extensive surface area, providing good binding sites for urea molecules .

Activated Carbon can be regenerated and reused many times which helps in reduction of cost compared to using fresh carbon each time. This feature not only saves resources but also help in preventing environmental damage by reducing waste generation and carbon footprint.

TABLE 1: CHARACTERISTICS OF ACTIVATED CARBON

Carbon Content	High Carbon content, typically over 90%				
Specific Surface Area	Large Surface Area, often exceeding 1000m <sup>2</sup> /g				
Porosity	High Level of Porosity with various pore size				
Adsorption Capacity	Exceptional adsorption capacity for a wide range of				
	substances				
Thermal stability	High Thermal Stability, withstand elevated				
	temperatures without significant degradation				
Surface Chemistry	Surface may be modified to enhance selectivity for				
	specific adsorption processes				
Environmental Benefits	Environmental friendly, often sourced from renewable				
	materials like coconut shells, wood, or coal.				

### 2.2 Ruthenium (Ru) as a Catalyst for Ammonia Decomposition

Ruthenium (Ru) is a highly effective catalyst employed in the ammonia decomposition process, which plays a significant role in various industrial applications. Its remarkable catalytic properties stem from its unique electronic structure and surface characteristics. Ruthenium-based catalysts exhibit exceptional catalytic activity, stability, and selectivity during the decomposition of ammonia (NH<sub>3</sub>) into its constituent gases, nitrogen (N<sub>2</sub>) and hydrogen (H<sub>2</sub>).

One key advantage of ruthenium catalysts is their ability to operate efficiently at moderate temperatures and pressures, making them suitable for a wide range of applications. Moreover, ruthenium-based catalysts are highly resistant to poisoning, a common issue in catalytic processes,

which means they maintain their catalytic activity over an extended period, resulting in prolonged catalyst lifespan.

### 3 Methodology

The process outlined for harnessing energy from urea found in human urine comprises three primary stages. Initially, urea is extracted from an aqueous solution through its adsorption onto commercially available activated carbon. Following this, a thermal treatment is employed to rejuvenate the carbon adsorbent, simultaneously triggering the decomposition of urea into ammonia and carbon dioxide. Finally, hydrogen is generated by catalytically breaking down ammonia, serving as an energy source.

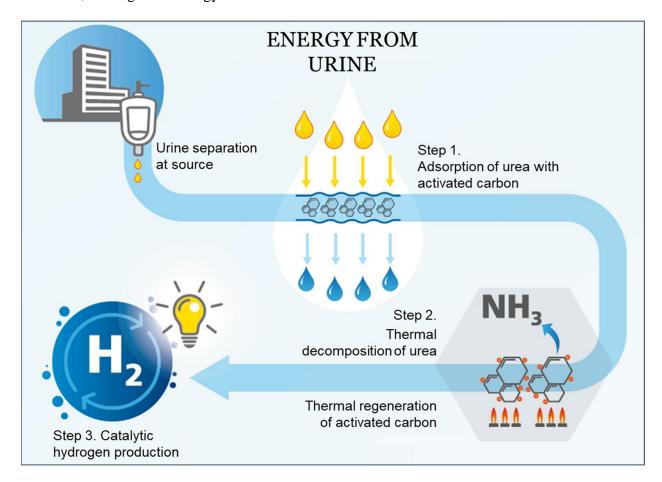


Figure 2: A Schematic of the suggested technique for obtaining energy from separate Wastewater Streams.

(https://www.sciencedirect.com/science/article/pii/S0043135422008788)

### 3.1 Step 1. Adsorption of urea from domestic wastewater

The initial stage of our process involves the utilization of activated carbon, a versatile and ecofriendly material, to separate urea from an aqueous solution efficiently. The adsorption process, our chosen method, effectively segregates urea from the solution, mitigating the need for energyintensive thermal treatments commonly found in industrial processes. Urea's propensity to behave similarly to water molecules and form hydrogen bonds presents challenges in its separation.

Experiments indicate that lower temperatures range of 30-60°C favors urea adsorption onto activated carbon, signifying an exothermic process as heat is released when urea molecule come into contact with activated carbon. However, urea's relatively low affinity for activated carbon due to its resemblance to water molecules remains a notable characteristic. Further analysis involved mathematical modeling, fitting the experimental data into each adsorption isotherm equations.

### 3.1.1 Different Isotherm Equations

A urea adsorption isotherm was created by plotting equilibrium concentration  $C_e(mg/L)$  versus the adsorption quantity  $q_e(mg/g)$ , and fitting was done at different type of adsorption isotherm equation.

First, research have performed on Langmuir adsorption isotherm equation and observed that the obtained  $R^2$  value was very low (0.364).

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

As correlation with the Langmuir was low .The Freundlich adsorption isotherm equation is used and the  $R^2$  value obtained was very high(0.996). Therefore, there was a high correlation with the Freundlich formulae.

$$log q_e = log K_F + \frac{1}{n} log C_e$$

Further Dubinin-Redushkevich(D-R) adsorption isotherm equation is fitted and the R<sup>2</sup> valve obtained was low(0.692). urea adsorption did not follow the D-R formulae.

$$log q_e = log q_m - Be^2$$

The Temkin adsorption isotherm equation is fitted and  $R^2$  valve was low (0.822);therefore, urea adsorption does not follow Temkin formulae.

$$q_e = \frac{RT}{h} \ln \left( K_T C_e \right)$$

The Harkins-jura adsorption isotherm equation is fitted and the  $R^2$  valve of the plot was low(0.571); therefore, urea adsorption does not follow Harkins-jura formulae.

$$\frac{1}{q_e^2} = \left[\frac{B}{A}\right] - \left[\frac{1}{A}\right] \log C_e$$

The Hasley adsorption isotherm equation is fitted and the  $R^2$  valve after plotting was very high (0.996).

$$lnq_e = \left[ \left( \frac{1}{n} \right) lnk \right] - \left( \frac{1}{n} \right) lnC_e$$

From the <u>Table 1(Kameda 2020</u>) of  $R^2$  value obtained from different adsorption isotherms for urea. One can conclude that the urea adsorption onto activated carbon is best fitted for the Freundlich and Halsey formulae, as they show the maximum  $R^2$  value.

TABLE 2: CORRELATION COEFFICIENT OF EACH ADSORPTION ISOTHERM FOR UREA

Urea	Langmuir	Freundlich	Dubinin- Redushkevich	Temkin	Harkins- Jura	Halsey
$\mathbb{R}^2$	0.364	0.996	0.692	0.822	0.571	0.996

### 3.2 Step 2. Desorption and decomposition of urea

After successfully adsorbing urea onto activated carbon from the aqueous solution, the next crucial step involves regenerating the adsorbent for reuse while simultaneously releasing the captured urea. This regeneration process relies on thermal treatment at 250°C, which serves the dual purpose of activating carbon and facilitating urea decomposition.

Urea typically decomposes within the temperature range of 130 to 200°C, resulting in the production of ammonia (NH<sub>3</sub>) and isocyanic acid (HNCO) according to <u>R.1</u>, starting at 133°C. The isocyanic acid can then undergo hydrolysis, further converting it into NH<sub>3</sub> and CO<sub>2</sub> following R.2.

$$(NH_2)CO(NH_2)(s) \to NH_3(g) + HNCO(g)$$
 (R.1) 
$$HNCO(g) + H_2O(g) \to NH_3(g) + CO_2(g)$$
 (R.2)

Temperature-programmed desorption (TPD) experiments were conducted to assess the production of ammonia, isocyanic acid (HNCO), and carbon dioxide (CO<sub>2</sub>) during the thermal decomposition of urea. Ammonia is generated between 130 and 200°C, aligning with the decomposition

temperature of solid urea. Notably, HNCO is not observed within this temperature range, suggesting that most of the HNCO undergoes hydrolysis due to the presence of interstitial water trapped within the activated carbon(Asiain-Mira, 2022)

Additionally, an increase in CO<sub>2</sub> production is observed for the saturated activated carbon compared to the fresh one, providing further evidence of HNCO hydrolysis. Furthermore, Decomposition of by-products formed during the thermal decomposition, such as cyanuric acid can be decomposed to HNCO at temperature range of 250 and 275°C.

In summary, the proposed mechanism for the decomposition of urea adsorbed on activated carbon involves the thermal decomposition of adsorbed urea into NH<sub>3</sub> and HNCO between 130 and 200°C. Most of the HNCO undergoes hydrolysis, resulting in the generation of additional NH<sub>3</sub> and CO<sub>2</sub>. Some HNCO may also undergo side reactions, leading to the formation of by-products like biuret( $C_2H_5N_3O_2$ ) and cyanuric acid. Indeed, Schaber et al. (2004) found that cyanuric acid decomposes between 250 – 275 °C into HNCO, following R.3 (Schaber et al., 2004), which perfectly matches with the HNCO profile found herein.

$$C_3H_3N_3O_3(s) \rightarrow 3 \ HNCO \ (g)$$
(R.3)

### 3.3 Step 3. Catalytic decomposition of ammonia into hydrogen

Thermal decomposition of urea achieved in step 2 was coupled with catalytic decomposition of ammonia using ruthenium catalyst supported on carbon nanotubes in step 3.Two reactors are connected in series (Fig. 2). In first reactor a bed of saturated activated carbon is placed which is operated at 200°C for desorption of urea and decomposition into ammonia. In second reactor consist of Ru/CNT used as catalyst for ammonia decomposition at the temperature of 400°C. High temperature is maintained to ensure a high level of ammonia decomposition conversion (Hill and Torrente-Murciano, 2014).

Decomposition of ammonia at 400°C produces nitrogen and hydrogen. After its hydrogen can be separated from nitrogen by using different methods such as Membrane separation using palladium which passes hydrogen through it other can be cryogenic separation as hydrogen (-252.87°C) has lower boiling point then nitrogen (-195.79°C).

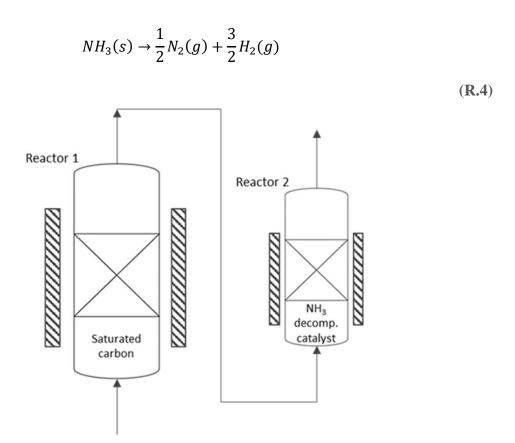


Figure 3: Schematic of Catalytic decomposition of ammonia into hydrogen (https://www.sciencedirect.com/science/article/pii/S0043135422008788)

### 3.3.1 Equilibrium Decomposition curve of Ammonia

Using DWSIM software, we created an equilibrium reactor for the decomposition of ammonia (as shown in Fig 3(A)) using an equilibrium conversion reaction (R.4). After running the flowsheet, we collected data by increasing the temperature at various pressure conditions of 1 bar, 4 bar, 40 bar, and 80 bar. We then used Excel to plot the curve depicting the mole fraction of ammonia decomposition (as illustrated in Fig 3(B)).

$$2NH_3 <=> N_2 + 3H_2$$
 (R.5)

From the results, one can conclude that it is an endothermic process. Therefore, increasing the temperature favors the decomposition of ammonia, while the equilibrium conversion of ammonia decreases with an increase in pressure.

A high yield or complete conversion in the ammonia decomposition process requires elevated temperatures and reduced pressures. Conversely, ammonia synthesis, the reverse reaction, benefits from lower temperatures and increased pressures.

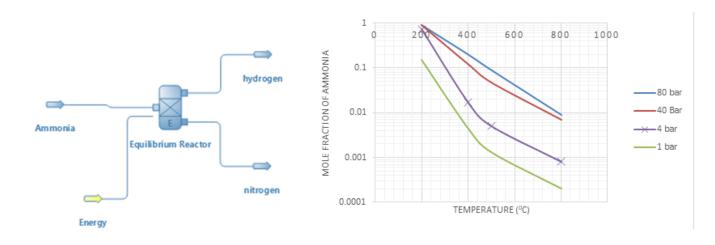


FIGURE 4: (A) DWSIM FLOWSHEET FOR EQUILIBRIUM CONVERSION OF AMMONIA .(B) EQUILIBRIUM MOLE FRACTION OF AMMONIA AT 200–800 C AND DIFFERENT PRESSURE 1,4,40,80 BAR

### 4 Conclusion

In conclusion, one can efficiently extract hydrogen from wastewater by adsorbing urea onto activated carbon at relatively low temperatures ranging from  $30 \text{ to } 60^{\circ}\text{C}$ , followed by thermal urea desorption and decomposition at  $250^{\circ}\text{C}$ . This thermal process regenerates the carbon while maintaining a consistent adsorption capacity. Moreover, the study included fitting various adsorption isotherms, and the results indicated that both the Freundlich and Halsey formulas produced the highest  $R^2$  values.

Subsequently, ammonia is decomposed at 400°C in the presence of a Ru/CNT (Ruthenium on Carbon Nanotubes) catalyst, resulting in the production of hydrogen as an energy fuel. It's worth noting that the equilibrium conversion of ammonia during this process is endothermic; thus, increasing the temperature favors the decomposition of ammonia, while an increase in pressure leads to a decrease in the equilibrium conversion of ammonia.

This method introduces a novel perspective on hydrogen production, as it enables the recovery of hydrogen from segregated wastewater streams, offering potential benefits in terms of both sustainability and energy utilization.

### 5 Future Work

In Future we would like to focus on:

- Energy Balance Calculation: To calculate energy efficiency of hydrogen process by conducting energy balance calculation, considering energy inputs, losses and the overall energy yield.
- Process Simulation: Perform detailed process simulations under varying conditions, such as temperature, and flow rates.
- Adsorber Design: To develop an effective adsorber for urea adsorption and hydrogen generation.
- Feasibility Study: Investigate whether production of hydrogen from wastewater stream will be feasible or not at the large scale.

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