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Energy Conversion and Management, 2020; 210:112709-1-112709-13

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Final publication at: <http://dx.doi.org/10.1016/j.enconman.2020.112709>

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**14 April 2022**

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# Thermodynamic potential of a novel plasma-assisted sustainable process for co-production of ammonia and hydrogen with liquid metals

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## Abstract

In the present article, the thermodynamic potential of a novel nitrogen fixation process for co-production of ammonia and hydrogen is investigated. The developed process employs a liquid metal such as gallium to drive nitrogen fixation reactions using three reactors including reactor R<sub>1</sub> to produce gallium nitride from gallium and nitrogen, reactor R<sub>2</sub> to produce ammonia and hydrogen from gallium nitride, and a plasma reactor R<sub>3</sub> to convert gallium oxide to pure gallium. The results of the thermodynamic assessments showed that the proposed reactions are spontaneous and feasible to occur in the reactors. Likewise, the first two reactions are exothermic with  $\Delta H = -230 \frac{\text{kJ}}{\text{mol}}$  and  $\Delta H = -239 \frac{\text{kJ}}{\text{mol}}$  in reactors R<sub>1</sub> and R<sub>2</sub>, respectively with equilibrium chemical conversion of 100%. The plasma reactor requires thermal energy to drive an endothermic reaction of gallium oxide dissociation with  $\Delta H = +870 \frac{\text{kJ}}{\text{mol}}$ . Thermochemical equilibrium analysis showed that the molar ratio of steam to GaN, pressure and temperature of the reactor R<sub>2</sub> are determining operating parameters identifying the final product of reactor such that by increasing the temperature, the ratio of hydrogen to ammonia ( $\psi$ ) increases. However, by increasing the molar ratio of steam/GaN ( $\phi$ ), the ratio of hydrogen to ammonia promotes reaching 70% pure H<sub>2</sub> at 673 K at  $\phi=1.0$ . Then  $\phi$  is decreased due to the unreacted steam appeared in the product. The equilibrium chemical conversion of all reactors is expected to reach the completion point ( $\chi=100\%$ ) due to the highly negative Gibbs free energy of the liquid metal-based reactions and potentially due to the catalytic effect of the liquid metal together with high heat and mass transfer coefficient offered by liquid metals at high temperatures.

**Keywords:** Nitrogen fixation, ammonia production, hydrogen production, thermal plasma reactor, liquid metals.

## 1. Introduction

Energy production is one of the critical sectors in the development of a robust and dynamic economy of developed and developing countries, which can cause environmental pollution due to the consumption of fossil fuels. A census has been reached that despite efforts made to develop new technologies based on hybridisation with renewable energy resources, fossil fuels will remain the main energy supply for the next two decades. Combustion is one of the well-established methods to release the energy content of fossil fuels, which is associated with the production of greenhouse gases (GHG) and release of particulate materials (PM<sub>2.5</sub>), CO<sub>2</sub> and other environmental pollutants. PM<sub>2.5</sub> strongly contributes to the increase in the number of patients with lung and gastric cancers, while CO<sub>2</sub> is the main component severely affecting global warming and world climate change. Therefore, there is a need for further investigation aiming at developing new processes for the production of clean fuels such as hydrogen, while decreasing the emission of GHG and pollutants to the environment.

Hydrogen is by far one of the promising clean fuels, which can be a replacement for fossil fuels. Hydrogen with lower heat value (LHV) of 120 MJ/kg, can produce water vapour during the combustion process, which in turn lowers the emission of carbon dioxide. In comparison with fossil fuels, hydrogen offers a higher LHV value, (e.g. 50 MJ/kg for natural gas vs. 120 MJ/kg for H<sub>2</sub>). This can improve the thermal and energetic performance of the engines and processes and reduce the costs associated with the design of the burners, reactors and combustors. The current pathway for the production of hydrogen is through reforming of natural gas, which is an energy-intensive process. Apart from the energy aspect, the reforming process delivers a large amount of CO<sub>2</sub> production to the environment as the process requires several reactors to increase the chemical conversion extent. To suppress the emission of greenhouse gases, catalytic reforming process was developed to lower the operating temperature, while suppressing the emission of GHG by increasing the chemical conversion of the reforming reaction. Despite promising outcomes, the presence of the catalyst in the reactor is associated with challenge such as carbon deposition, catalyst sintering and deactivation, increasing the operating cost and complexity of the process. The challenges are more intensified when catalysts require regeneration, which produces a large quantity of CO<sub>2</sub> and CO.

Another commercial pathway for the production of hydrogen is to utilise water electrolysis cells, which can also be hybridised with renewable energy to promote the economic viability

of the process. Despite the hybridisation potential, the electrolysis cell has a low chemical efficiency (20 to 40%) but high energy efficiency. Also, the challenges associated with the use of electrolysis such as robust energy storage for continuous production together with the corrosion of the electrodes require further investigation. Such challenges are the main barrier against the improvement in the technology readiness level of the electrolysis.

Apart from the production route, storage and safely transfer of hydrogen is another issue associated with the production of hydrogen at large scale and for industrial section. Hydrogen is a flammable and explosive gas and requires specific levels of safety for the storage and use, which are costly. Thus, recently special attention has been paid to the production of hydrogen carriers such as metal aldehydes and ammonia. Such carriers can directly be used as a fuel, intermediate product or chemical components or can safely be transferred to the end-user site. Currently, the safety measures have been developed for the transfer of ammonia from production sites to the consumption plants.

Ammonia ( $\text{NH}_3$ ) is commercially produced through the nitrogen fixation driven by Harber-Bosch process (HB), which is an energy intensive process requiring high pressure to shift the equilibrium point inside the reactor. Also, a catalyst with a high specific surface area is employed inside the reactor to increase the chemical conversion extent of the reaction. The HB process has extensively been studied in the literature and it has already reached its efficiency's theoretical limitation. Hence, further investigation aiming at decreasing the energy consumption of the process is not conducted as it is not economically viable. To bypass the challenges associated with the HB process, nitrogen fixation via sustainable chemical processes is one potential approach, which not only reduces the energy consumption associated with the process, but also increases the chemical conversion extend and economic viability of the ammonia production process. In a sustainable process, not only the side products, but also the energy produced in the process can be consumed by the process itself, while lowering the potential emission of GHG and environmental pollutants (e.g.  $\text{CO}_2$ , CO and  $\text{H}_2\text{O}$ ). Also, depending on the quality and type of the end-user, the product of a sustainable process can be altered by a change in the operating parameters of the reactors.

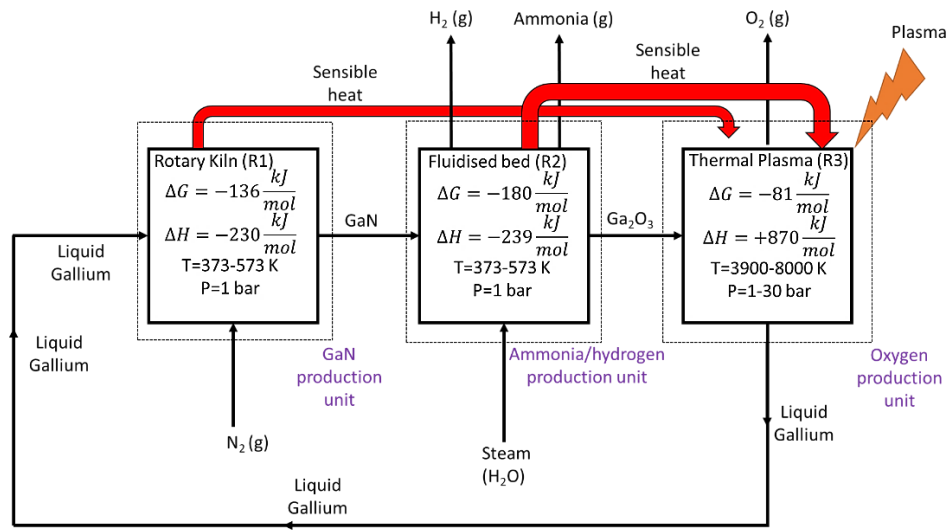
In order to develop a sustainable process, the reactions should thermodynamically be feasible to occur. For some reactions, due to the highly positive Gibbs free energy of the reaction ( $\Delta G$ ), conventional reactors are unable to drive the reaction. Hence, a specific type of reactor

is required to maintain the required energy level for driving the reactions. Plasma reactor is one potential option, which can provide plausible heat and mass transfer medium, by consuming low energy in comparison with conventional reactors. Plasma is the fourth state of the matter, which includes atoms, molecules, ions, cations, and electrons together with heavy particles. Despite the charged species, the plasma environment is neutral. The plasma reactor can be categorised into different classifications of thermal plasma (hot, equilibrium) and non-thermal plasma (cold, non-equilibrium), which both have their advantages and disadvantages. The main feature of a plasma reactor regardless of its type is to provide conditions to drive reactions with super positive Gibbs free energy. If a hot plasma is used, almost all the reactive species have the same temperature and the conversion of the reactor approaches the equilibrium conversion extent. However, for a cold plasma, of course, the chemical conversion is far from the equilibrium value, however from the economic and energetic performance point of view, the energy consumption for the cold plasma is lower than that of hot plasma. In order to justify the use of a cold plasma reactor for the sustainable process, it is required to promote the performance of the reactor with passive techniques such as using catalysts, magnetic fields and super-porous nano-electrodes. Therefore, plasma technology opens a new door for driving reactions that cannot be driven in a conventional reactor.

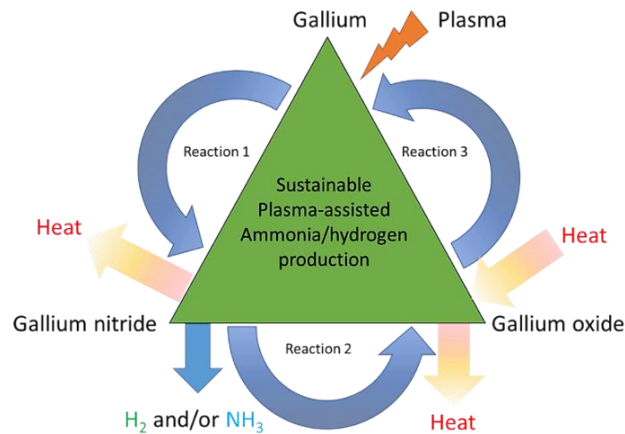
In light of the above, designing a sustainable process for ammonia production through nitrogen fixation via plasma reactor can potentially be an alternative to the current ammonia production pathways. It can also offer low energy consumption (if a cold plasma is used) and a high chemical conversion extent if a cold plasma reactor with a catalyst or a hot thermal plasma is utilised in the process. In the present work, using the potential of plasma environment and plausible heat and mass transfer characteristics of liquid metals (here gallium), a new process is developed to take advantage of nitrogen fixation reaction for the co-production of hydrogen and ammonia using a green process, which does not produce any GHG. Thanks to the features of the plasma, the sustainability of the process is guaranteed. A thermochemical equilibrium model is developed to evaluate the effect of different operating parameters including the feed ratio, temperature and pressure on the products of the reactors. The thermodynamic stability phase diagram of the gallium in reaction with other components is also studied and best operating condition is obtained using response surface methodology.

## **1. Conceptual process design**

Figure 1 presents the schematic diagram of the process proposed for the co-production of hydrogen and ammonia using liquid metal and a plasma reactor.



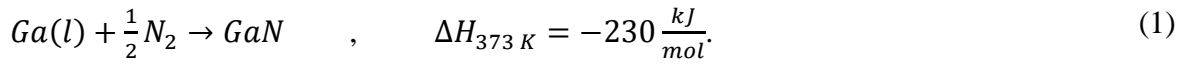
**Fig. 1a.** Schematic illustration of the sustainable proposed process for co-production of ammonia and oxygen.



**Fig. 1b.** A schematic diagram of the sustainable process proposed in the present research.

In the present work, gallium (Ga) is proposed to be used as liquid metal and a medium for chemical reaction, which does not require high temperatures to form a stable liquid metal phase. Another advantage of gallium is that it is not corrosive at low temperatures. The melting temperature of gallium is  $29.7\text{ }^{\circ}\text{C}$  ( $302.7\text{ K}$ ), which is not solidified at ambient temperature or might need a trace heating during winter when the room temperature is less than the melting point of gallium. The proposed system uses three reactors including reactor  $R_1$  for gallium nitride ( $GaN$ ) production from gallium ( $Ga$ ) and nitrogen ( $N_2$ ), reactor  $R_2$  for ammonia, hydrogen and gallium oxide ( $Ga_2O_3$ ) production from  $GaN$  and steam ( $H_2O$ ), and

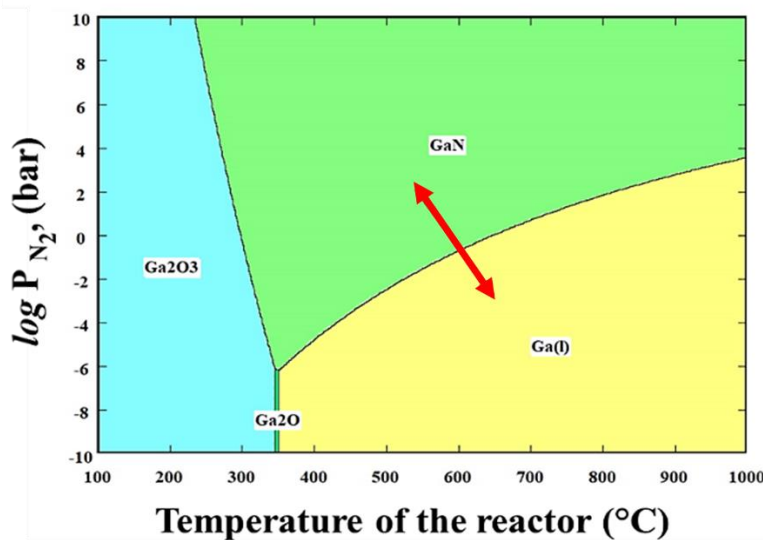
reactor R<sub>3</sub> for dissociation of Ga<sub>2</sub>O<sub>3</sub> and reproduction of gallium, which offers the sustainability of the process. In reactor R<sub>1</sub>, the following reaction occurs:



The above equation is exothermic and the released thermal energy can partially be transported to another reactor using sensible heat carried by GaN solid particles. Due to the nature of the product, which is a slurry of liquid gallium and solid particles, a kiln rotary reactor is proposed which can offer the following advantages:

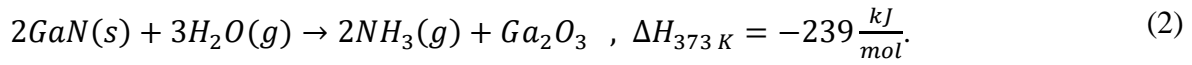
- 1) Sufficient residence time for contact between the gas, liquid and solid particles;
- 2) Great heat and mass transfer coefficient by providing effective rotating speed;
- 3) Capability to handle the continuous operation;
- 4) Compatibility to operate at low, mid- and high-temperature conditions;
- 5) High technology readiness level (commercially available).

The stability phase diagram of the gallium-nitrogen-oxygen thermodynamic system has been simulated with HSC chemistry software package and is depicted in Figure 2. As can be seen, at temperature ranged between 373 K and 573 K, for an environment pressurised with nitrogen, the stable thermodynamic phases are GaN and Ga (l). Hence, a mixture of the components is expected to leave the reactor in the form of a slurry. With sufficient injection of nitrogen and an optimised ratio of N<sub>2</sub>/Ga molar ratio, the final product of the reactor is GaN, which can be fed into reactor R<sub>2</sub>.



**Fig. 2.** The stability phase diagram of Ga-N-O thermodynamic system in reactor R<sub>1</sub>.

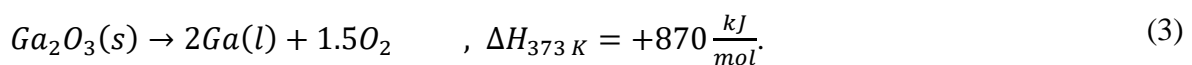
In reactor R<sub>2</sub>, the produced GaN reacts with steam to drive the nitrogen fixation reaction using the following reaction:



Reaction 2 is highly exothermic and the temperature can be self-maintained in the reactor once steam is injected in the system. The steam injection can provide a plausible mixing, while mainlining the temperature required for the reaction. It is worth saying that the morphology of the GaN particles can be non-uniform due to the operating conditions of rotary kiln, thereby requiring a relatively robust heat and mass transfer system to drive the reaction to the completion point. That being said, solid particle fluidised bed is one potential reactor, which can offer the following advantages:

- 1) Uniform mixing between the particles and gases, which results in the uniform heat and mass transfer due to the sufficient collision of particles;
- 2) Symmetric and uniform temperature distribution along with the length and diameter of the reactor;
- 3) Capability to operate continuously;
- 4) Capability to separate carried-over particles by recovering and returning them to the reactor;
- 5) Ability to operate at various particle distribution size and morphology.

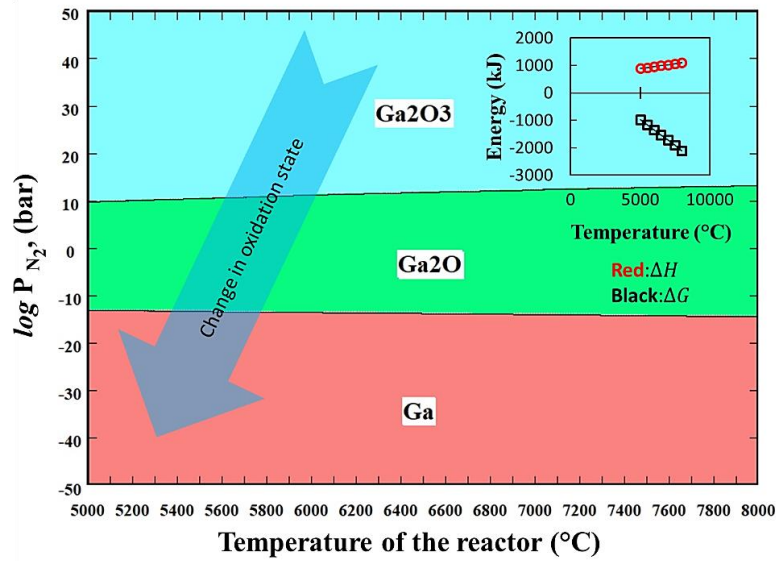
The outlet from reactor 2 is fed into the plasma reactor (reactor R<sub>3</sub>), in which the gallium oxide, which is a component with high positive Gibbs free energy is dissociated to liquid gallium and oxygen according to the following equation:



Notably, the oxygen released from the process can be used in other applications, which promotes the economic viability of the process. The oxygen produced by the proposed process potentially requires less energy in comparison with air separation units and water splitting technologies, however, to prove this a techno-economic assessment must be conducted on the process once the energy requirement of the process is experimentally verified and evaluated. This is beyond the scope of the present investigation.

[Figure 3](#) represents the thermodynamic stability diagram of the gallium-oxygen system for the plasma reactor to dissociate gallium oxide particles. As can be seen, the Gibbs free energy of the reaction is negative at  $T > 5000$  K, while the reaction is highly endothermic requiring

~1000 kJ/mol of energy to drive the reaction. Also, the stable phases are Ga<sub>2</sub>O and Ga. Notably, Ga<sub>2</sub>O can also be dissociated to Ga by reducing the partial pressure of oxygen and nitrogen in the system. Normally, this can be done using a sweeping gas such as argon. Hence, the reactions in reactor R<sub>3</sub> is feasible at a minimum temperature of ~3500 K, however, the equilibrium chemical conversion at this temperature barely reaches ~40%. At T > 5000 K, the equilibrium chemical conversion extent reaches 100%.



**Fig. 3.** The calculated stability phase diagram of Ga-N-O thermodynamic system in reactor R<sub>3</sub>.

## 2. Methodology

To estimate the net enthalpy and the value of Gibbs free energy change for each reaction, the following equation was utilised:

$$\Delta M_{rxn} = \sum_{prod} \Delta M_i^f(T) - \sum_{react} \Delta M_i^f(T). \quad (4)$$

Here,  $M$  is a surrogate for either the enthalpy of the reaction, or the Gibbs free energy value belonging to component  $i$ . Also, the term  $\Delta M_i^f(T)$  is either the net enthalpy of formation of component  $i$  or its Gibbs free energy of formation calculated at operating temperature of  $T$ . The subscripts “ $rxn$ ”, “ $react$ ” and “ $prod$ ” stand for the term “reaction”, “reactants” and “products”, respectively. To conduct the simulations, Aspen Plus software package together with HSC chemistry 7.0 were employed using Gibbs minimisation method approach. For the plasma reactor, any reactive species including ions, cations and free electrons were taken into

consideration. The valid phases were solid, liquid, gas, ion, cation and free electrons and/or positron. The thermochemical equilibrium module of HSC Chemistry together with R-Gibbs reactor were interlinked and used to assess the equilibrium performance of the plasma reactor. To calculate the thermo-physical properties of the components including heat capacity, standard enthalpy of formation, standard Gibbs free energy and density, Aspen properties and Hysys software packages were used. The properties were verified against the data bank reported in Barin handbook. Uniquac and Peng-Robinson thermodynamic equation of states were employed and the estimated results were within  $\pm 0.5\%$  of agreement with each other.

### 3. Results and discussion

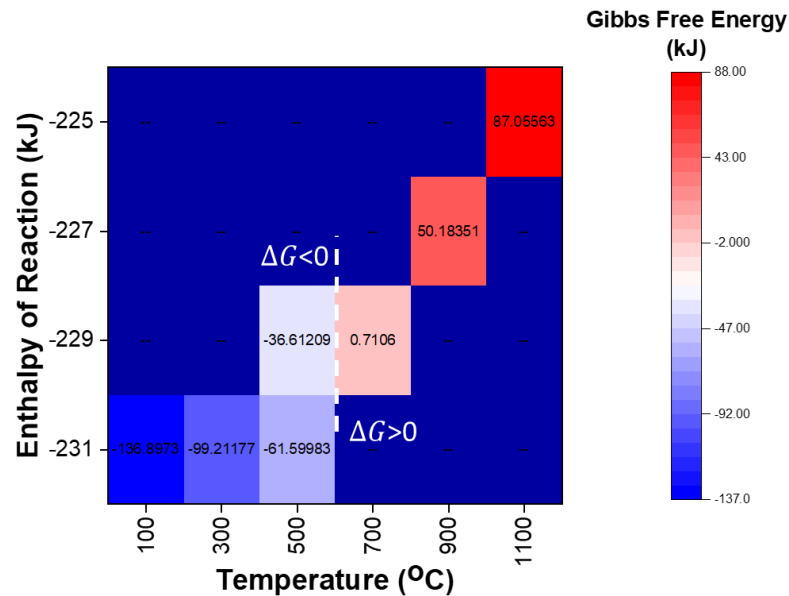
A series of thermodynamic equilibrium models were developed to assess the thermodynamic potential of the proposed process for the co-production of hydrogen and ammonia. In the following sub-sections, the effect of different operating parameters on thermodynamic performance and thermodynamic properties of the system is discussed.

#### 3.1. Reaction's Gibbs free energy

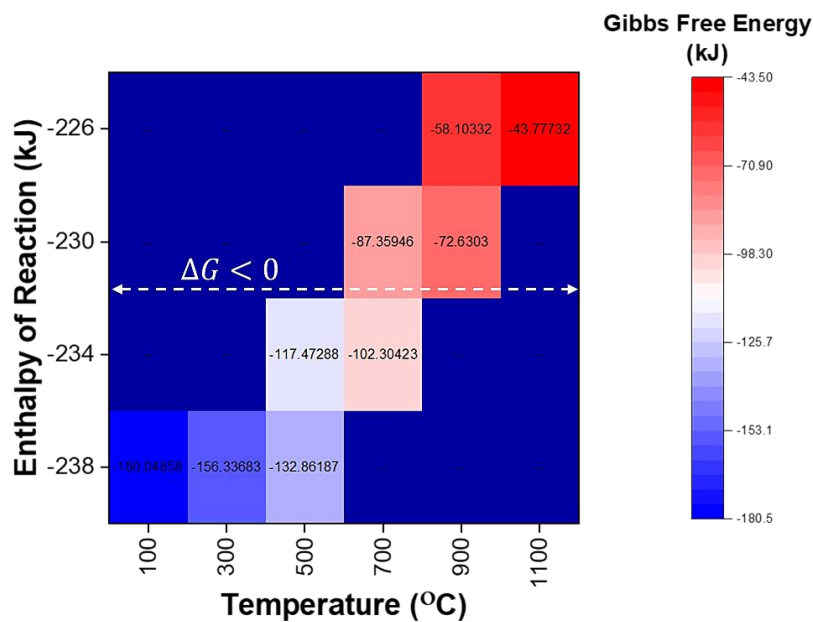
Figure 4 presents the variation of the calculated Gibbs free energy and enthalpy of reaction on the operating temperature of the reactor  $R_1$ . As can be seen, the change in Gibbs free energy of the reaction is negative within the operating temperatures of  $373\text{ K} < T < 873\text{ K}$ . Within the identified range of temperature, the reaction is spontaneous and the chemical equilibrium conversion reaches the completion point. For example, at  $T=573\text{ K}$ ,  $\Delta G = -99.2 \frac{\text{kJ}}{\text{mol}}$  reaching  $-61.6 \frac{\text{kJ}}{\text{mol}}$  at  $773\text{ K}$ . From  $873\text{ K}$ ,  $\Delta G > 0$ , thereby requiring a non-conventional reactor to handle the reaction. Interestingly, within the above temperature range, the enthalpy of reaction is highly negative e.g.  $\Delta H = -225 \frac{\text{kJ}}{\text{mol}}$  to  $-231 \frac{\text{kJ}}{\text{mol}}$ , showing that the reaction is exothermic. It is worth saying that the thermal energy released in the reactor can be partially transported to the second reactor through sensible heat transfer carried by GaN particles with the heat capacity of  $0.49\text{ J/(gK)}$  and thermal conductivity of  $0.8\text{-}1\text{ W/(mK)}$ .

Figure 5 represents the variation with temperature of the calculated enthalpy of reaction and the change in the Gibbs free energy of the reaction in reactor  $R_2$ . As can be seen, reaction is highly exothermic, while the reaction is spontaneously occurring within the operating temperature of  $373\text{ K} < T$ . For example, at  $T=573\text{ K}$ ,  $\Delta G = -156\text{ kJ/mol}$ , while reaching -

43 kJ/mol at  $T=1373$  K. Within the same temperature range, the enthalpy of reaction changes from -238 kJ/mol to -226 kJ/mol. Interestingly, the released thermal energy from both reactors  $R_1$  and  $R_2$  can be used to preheat the products before introducing them to the plasma reactor. This in turn reduces the thermal load of the plasma reactor, which promotes the energetic performance of the process.

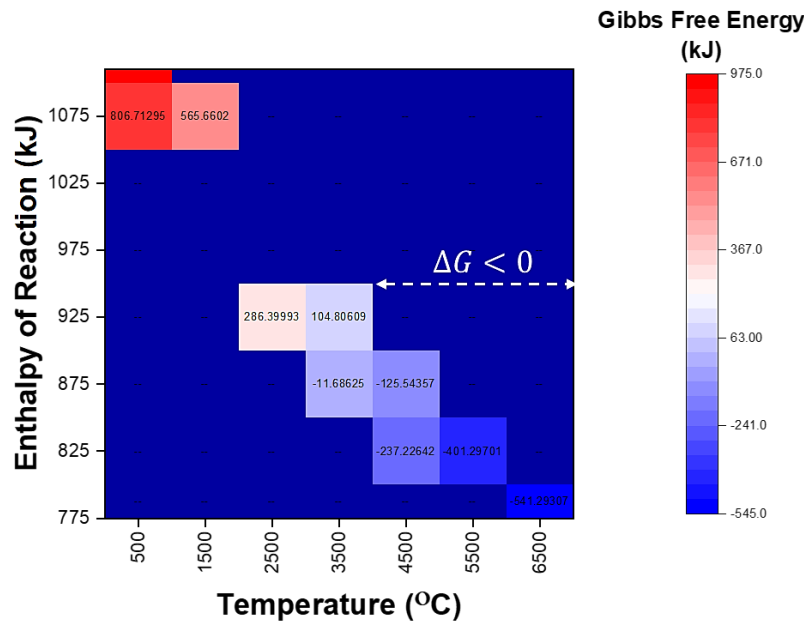


**Fig. 4.** The calculated dependence on temperature of the enthalpy of the reaction ( $\Delta H$ ) and the Gibbs free energy of the reaction ( $\Delta G$ ) in reactor  $R_1$ .



**Fig. 5.** The calculated dependence on temperature of the enthalpy of the reaction ( $\Delta H$ ) and the Gibbs free energy of the reaction ( $\Delta G$ ) in reactor  $R_2$ .

In Figure 6, the enthalpy and the change in the Gibbs free energy of the reaction in plasma reactor R<sub>3</sub> is depicted. As can be seen, the Gibbs free energy of the reactor is negative at  $T > 3500$  K showing that reaction 3 is thermodynamically feasible to occur in a plasma reactor. Also, the reaction is super endothermic requiring a large amount of heat to be dedicated to the reaction, although part of the heat can be supplied from reactors R<sub>1</sub> and R<sub>2</sub>. For example, at  $T=3500$  K,  $\Delta G = -11 \frac{kJ}{mol}$ , reaching  $\Delta G > -541 \frac{kJ}{mol}$  at  $T > 6500$  K.



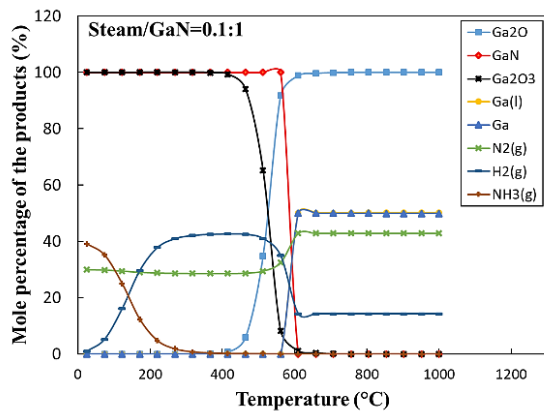
**Fig. 6.** The calculated dependence on temperature of the enthalpy of the reaction and the Gibbs free energy of the reaction in reactor R<sub>3</sub>.

Reactor R<sub>2</sub> as perceived from Figure 1 is the heart of the process by which the main products are produced, while reactor R<sub>3</sub> is a complementary element to close the chemical loop and guaranty the sustainability of the proposed process by dissociating Ga<sub>2</sub>O<sub>3</sub> to Ga, which cannot occur in a conventional reactor. Hence, these reactors are further investigated to identify the suitable operating parameters, in which the production of hydrogen and/or ammonia is maximised.

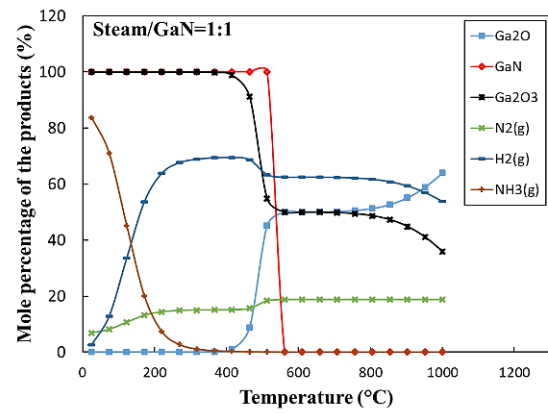
### 3.2.Reactor R<sub>2</sub>

Figure 7 represents the variation of the mole fraction of the products of reactor R<sub>2</sub> with the temperature of the reactor for various steam to gallium nitride molar ratios ( $\varphi$ ). As can be seen, regardless of  $\varphi$ , within the operating temperature range of  $373 \text{ K} < T < 673 \text{ K}$ , the main product of the reactor is ammonia, Ga<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>, therefore, this can plausibly be the optimised operating temperature for this reactor. For example, at  $\varphi=0.1$ , the mole fraction of

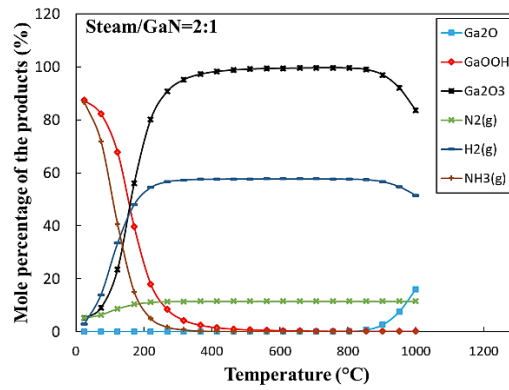
hydrogen changes from zero to ~40%, while that of ammonia decreases from ~41.5% to zero. Hence, there is a thermodynamic equilibrium trade-off behaviour identified between the production of hydrogen and ammonia in reactor R<sub>2</sub> such that the final product of the reactor can be regulated depending on the end-user needs, storage facility and the application of the fuel by changing the operating conditions of the reactor. Interestingly, by increasing  $\phi$  to 1.0, the production of ammonia and hydrogen is promoted to ~81% at 373 K (for ammonia) and ~70% (for hydrogen) at 673 K. With further increase in  $\phi$  value, the unreacted steam appears in the outlet of the reactor, which in turn decreases the mole fraction of the target products, while adding an extra thermal load to the process. This is because water should be eliminated from the products before they can be fed into the plasma reactor. This requires a robust heat exchanger to recover the steam and inject it back to the reactor. This factor can considerably affect the economy of the process since steam production can be expensive. It is worth saying that if the excess steam is not extracted from the reactor, a side reaction between gallium and steam proceeds resulting in the production of GaOOH, which is an amorphous stable phase of gallium hydroxide. The presence of GaOOH in the plasma reactor can produce H<sup>+</sup>, which aggressively attacks other ions and molecules due to the “ionisation impact” in the reactor. Hence, there is an optimum point for the ratio, which can be identified through optimisation or experiments.



(a)



(b)

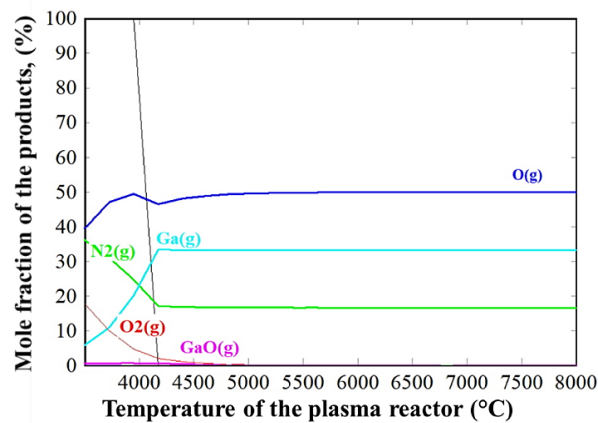


(c)

**Fig. 7.** Results of the thermochemical equilibrium analysis of reactor  $R_2$  at various molar ratios of steam /GaN ( $\phi$ ), a)  $\phi = 0.1$ , b)  $\phi = 1.0$ , c)  $\phi = 2.0$ .

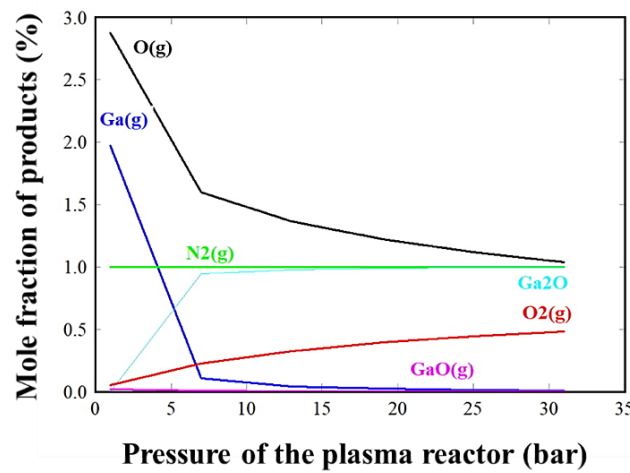
### 3.3.Reactor $R_3$

Figure 8 shows the calculated dependence of the mole fraction of the products of reactor  $R_3$  on temperature. As can be seen, the chemical conversion extent reached the completion point ( $\chi = 100\%$ ) for  $Ga_2O_3$  (the black line) by dissociating  $Ga_2O_3$  to Ga,  $Ga_2O$  and O (g). However, by increasing the temperature of the plasma regime,  $Ga_2O$  is further dissociated to Ga and  $O_2$ . Hence, the final product of the reactor is gallium and oxygen which should rapidly be quenched and separated. The oxygen can be used for further applications, while gallium is returned to the reactor  $R_1$  for nitrogen fixation reaction. Notably, at  $T > 5000$  K, reactor  $R_3$  reaches an equilibrium state in which gallium and oxygen are the main products with a constant mole fraction. Hence, this temperature is an optimum temperature for the plasma reactor.



**Fig. 8.** Variation of the mole fraction of the products on the temperature for the plasma reactor  $R_3$ .

In Figure 9, the effect of the pressure of the reactor on the mole fraction of the products of the reactor R<sub>3</sub> is depicted. As shown, by pressuring the plasma reactor, gallium oxide (Ga<sub>2</sub>O) forms massively in the reactor, which can add complexity to the operation of reactor R<sub>1</sub> once it is fed to the reactor. The formation of Ga<sub>2</sub>O creates a non-reactive phase of gallium, which does not participate in the reaction. Hence, there would be a need for making up the gallium content through an external stream of liquid metal, which would be a barrier against economic viability of the process by considering the fact that gallium is a scarce and expensive material. Commensurate with this, it is recommended no to pressurise the plasma reactor. Notably, it also reduces the production of oxygen as well, which in turn suppresses the advantage of oxygen production in the process.



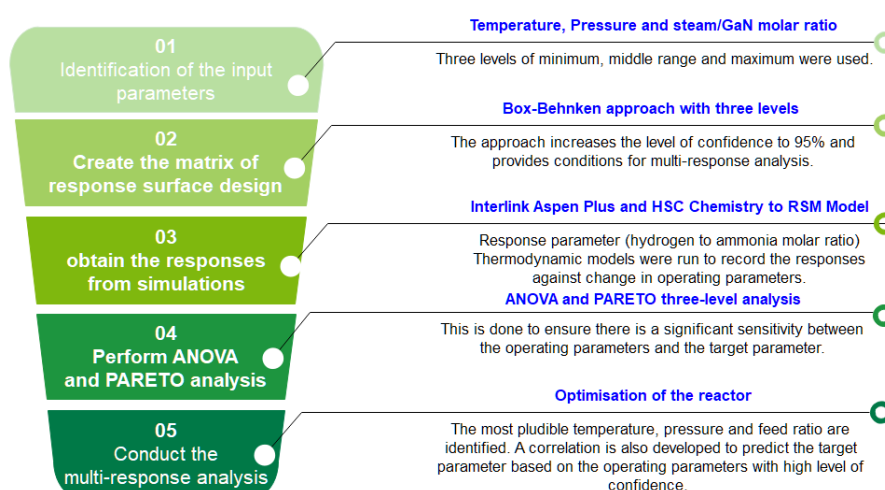
**Fig. 9.** Variation of the mole fraction of the products on the pressure of the plasma reactor R<sub>3</sub>.

### 3.4.Optimisation with response surface methodology

Response surface methodology (RSM) is a chain of statistical, mathematical and theoretical methods for design and optimisation of the complicated experiments and processes, where there is limited data obtained by simulations and/or experiments. An RSM model employs input parameters including operating conditions of the process and a target parameter to evaluate the sensitivity of the target parameter to those operating conditions and chooses the best ones, in which the target parameter is maximised or minimised. It is worth saying that the decision-making algorithm of the model strongly depends on the response of the system to a change in the operating parameters. The responses can be collected by experiments or by conducting high-fidelity simulations.

In the present work, we report the results of an optimisation based on Box-Behnken approach using RSM technique to identify the sensitivity of the production of ammonia and/or hydrogen to each of the operating parameters. Of course, only reactor R<sub>2</sub> was assessed as it is the heart of the process, directly determines the mole fraction of the products. Figure 10 shows the algorithm of solution for the RSM model developed in the present work. As can be seen, the algorithm of solution has five main stages. After creating the matrix of the model (stage 1 and 2), a series of simulations are conducted based on the operating conditions given in Table 1 developed by RSM. For each iteration, the response is collected from the simulation results and the optimisation is conducted once all twenty iterations are successfully conducted. It is worth saying that in the present work, the target parameter is the ratio of hydrogen to ammonia ( $\psi$ ).

### Algorithm of solution for developed RSM model



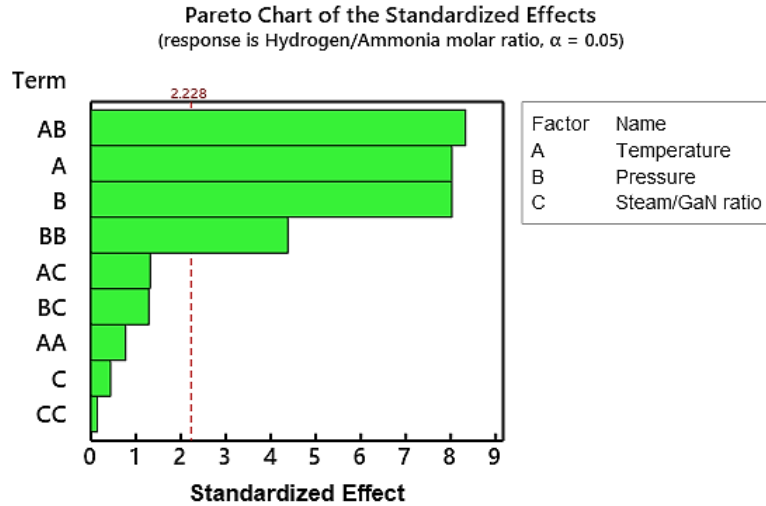
**Fig. 10.** Algorithm of the solution (flow diagram) for the RSM model developed in the present research.

According to the RSM model, initially, the input Table is created for temperature, pressure and steam/GaN molar ratio ( $\phi$ ) as identified in the thermo-chemical equilibrium analysis in the previous sections. As represented in Table 1, each operating parameter has three levels including minimum value (-1.0), middle value (0) and maximum value (+1.0). These values for temperature are 373 K, 523 K and 673 K, and for pressure are 1 bar, 15 bar, 31 bar, and for  $\phi$  are 0.1, 1.05 and 2, respectively.

**Table 1.** The response surface design matrix created with RSM model (randomized).

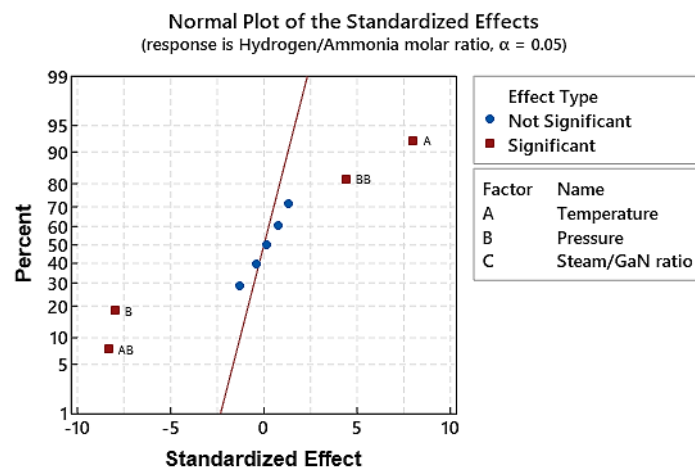
Run	Blk	Temp.	Press.	Steam/GaN
1	1	0.00000	0.00000	0.00000
2	1	-1.00000	1.00000	1.00000
3	1	1.00000	-1.00000	1.00000
4	1	0.00000	0.00000	0.00000
5	1	0.00000	1.00000	0.00000
6	1	0.00000	0.00000	1.00000
7	1	0.00000	0.00000	0.00000
8	1	1.00000	1.00000	1.00000
9	1	0.00000	0.00000	0.00000
10	1	1.00000	1.00000	-1.00000
11	1	-1.00000	1.00000	-1.00000
12	1	-1.00000	0.00000	0.00000
13	1	0.00000	0.00000	-1.00009
14	1	0.00000	-1.00000	0.00000
15	1	-1.00000	-1.00000	-1.00000
16	1	0.00000	0.00000	0.00000
17	1	1.00000	-1.00000	-1.00000
18	1	0.00000	0.00000	0.00000
19	1	-1.00000	-1.00000	1.00000
20	1	1.00000	0.00000	0.00000

Over twenty runs of simulations, the responses were recorded and used in the model to evaluate the sensitivity of the target parameter ( $\psi$ ) to the operating conditions. As can be seen in Figure 11, the Pareto analysis shows that the most important parameter is the temperature of the reactor  $R_2$ , which considerably affects its equilibrium chemical performance. As shown in section 4.2, to produce hydrogen and ammonia or combination of both, the temperature of the reactor must be narrowed down to a specific range. Also, a trade-off was identified between the production of ammonia and hydrogen. Hence, temperature was a key parameter in the equilibrium simulations, which was also identified by the Pareto analysis based on the RSM model as well. Interestingly, it was found that not only temperature (A), but also pressure (B) and an interaction between the temperature and pressure (AB) contribute to the performance of the reactor. Hence, through multi-response analysis, the sensitivity of the target parameter to the temperature and pressure of the reactor was assessed. Notably, the model identifies that the steam/GaN ratio ( $\varphi$ ) has no effect on the performance of the reactor. This parameter only determines which chemical component can be the dominant product of the reactor, which has already been identified through equilibrium analysis.



**Fig. 11.** The Pareto chart obtained with Response Surface Methodology for reactor R<sub>2</sub>.

Figure 12 represents the normal plot of the standardised effects of different operating conditions on  $\psi$  value for reactor R<sub>2</sub>. As can be seen, amongst all the potential interactions between the operating parameters (binary, ternary...), only temperature, pressure, and the interaction between temperature and pressure can affect the performance of the reactor, which is in-line with the results obtained from the Pareto analysis. Also, it is in accordance with the results obtained with ANOVA analysis, by which it was identified that the change in  $\psi$  value is significant when temperature and pressure values change in the reactor. Likewise, the values obtained for the standardised effects are far from the insignificance line (see Fig. 12), which confirms the justifications discussed in the previous sections. The detailed results of the ANOVA test are given in Table 2.



**Fig. 12.** The Effectiveness of different operating parameters on the target (molar ratio of hydrogen to ammonia) for reactor R<sub>2</sub>.

**Table 2.** Detailed results obtained from ANOVA analysis conducted on the sensitivity of the operating parameters on the target value.

Source	DF	Seq SS	Contribution	Adj SS	Adj MS	F-Value
Model	9	30711.9	96.06%	30711.9	3412.44	27.11
Linear	3	16009.4	50.08%	16232.0	5410.66	42.98
Temperature	1	8080.4	25.27%	8080.4	8080.37	64.19
Pressure	1	7864.3	24.60%	8077.6	8077.57	64.17
Steam/GaN ratio	1	64.8	0.20%	23.6	23.58	0.19
Square	3	5567.5	17.41%	5567.5	1855.85	14.74
Temperature*Temperature	1	2998.9	9.38%	75.0	74.97	0.60
Pressure*Pressure	1	2566.1	8.03%	2410.9	2410.88	19.15
Steam/GaN ratio*Steam/GaN ratio	1	2.5	0.01%	2.5	2.53	0.02
2-Way Interaction	3	9135.0	28.57%	9135.0	3044.99	24.19
Temperature*Pressure	1	8708.7	27.24%	8708.7	8708.70	69.18
Temperature*Steam/GaN ratio	1	218.3	0.68%	218.3	218.30	1.73
Pressure*Steam/GaN ratio	1	208.0	0.65%	208.0	207.98	1.65
Error	10	1258.8	3.94%	1258.8	125.88	
Source	P-Value					
Model	0.001					
Temperature ( <i>T</i> )	0.001					
Pressure ( <i>P</i> )	0.001					
Steam/GaN ratio ( <i>φ</i> )	0.674					
Temperature*Temperature	0.458					
Pressure*Pressure ( <i>PP</i> )	0.001					
Steam/GaN ratio*Steam/GaN ratio	0.890					
2-Way Interaction	0.000					
Temperature*Pressure ( <i>TP</i> )	0.003					
Temperature*Steam/GaN ratio	0.217					
Pressure*Steam/GaN ratio	0.228					

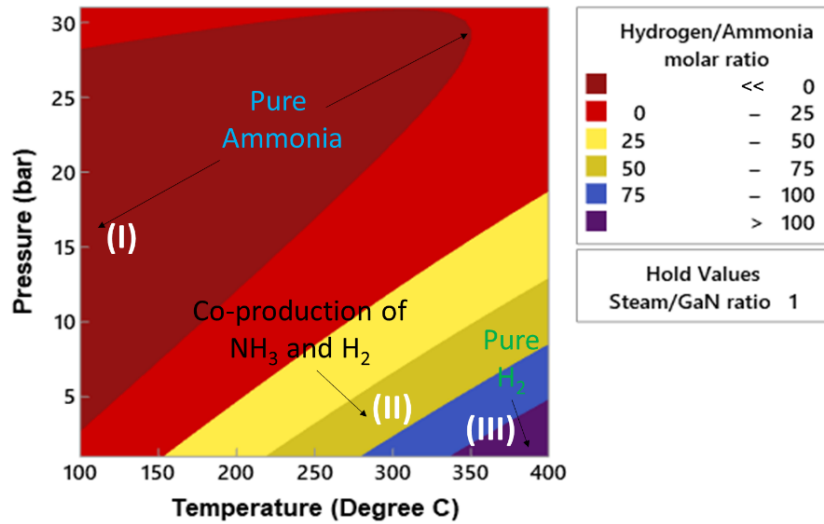
As can be seen in Table 2, the P-value for the temperature, pressure and their interaction is less than 0.05 showing that there is a meaningful correlation between these parameters and the  $\psi$  value. Also, the P-value for the general model is 0.001, which is again smaller than 0.05, showing that the developed ANOVA model is valid. Using regression analysis on the data obtained from the RSM model, the following equation was developed, which can predict the molar ratio of hydrogen to ammonia with R-square 0.97 with > 95% confidence interval:

$$(H_2:NH_3) \text{ ratio } (\psi) = -24.4 + 0.001 \times PP \times 0.348 \times T - 3.04 \times P + 0.5 \times \varphi - 0.014 \times TP \quad (5)$$

The developed equation correlates the  $\psi$  value to the most sensitive operating parameters. This can help one to predict the final composition of the product produced by reactor R<sub>2</sub> without a need to apply a thermochemical equilibrium and RSM models, which are time-consuming to be established and used.

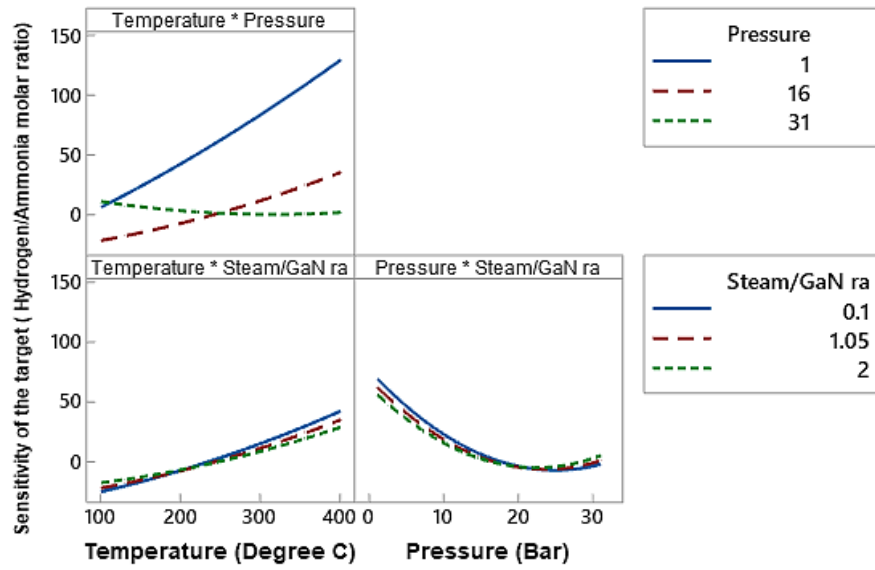
Figure 13 represents the effect of the binary interaction between the temperature and the pressure of the reactor R<sub>2</sub> on  $\psi$  value. As can be seen, three main regions are identified. In region I, in which 5 bar < *P* < 30 bar and *T* > 373 K, the equilibrium model shows that the dominant product of the reactor is ammonia together with small contents of hydrogen, which can be separated through a low-temperature condenser. In region II, which has lower

operating pressure (e.g. 5 to 10 bar), but higher temperatures (e.g. 473 to 573 K), the co-production of hydrogen and ammonia is thermodynamically feasible while in region III, for a non-pressurised reactor, at  $T > 573$  K, hydrogen is the main product.



**Fig. 13.** Dependence of the final product of the process on operating temperature and pressure of reactor R<sub>2</sub>.

Therefore, it is not recommended to pressurise reactor R<sub>2</sub> if the target product of the process is hydrogen. Figure 14 shows the calculated dependence of the sensitivity of  $\psi$  on the operating parameters of the reactor R<sub>2</sub>. As can be seen, the target parameter is super-sensitive to the temperature-pressure interaction ( $TP$ ) such that at a pressure of 1 bar, the sensitivity factor at  $T=473$  K is  $\sim 50$ , while it is suppressed to  $\sim 0.01$  at  $P=16$  and  $P=31$  bar. Also, by increasing the temperature of the reactor, the sensitivity of  $\psi$  to  $PT$  interaction increases, however, at  $P=31$  bar, the increase in the temperature of the reactor has no effect on the sensitivity factor. This means that at  $P > 30$  bar, the temperature of the reactor is not a key operating parameter and the performance of the reaction can be independent from the identified operating temperature range. For other interactions identified between the operating parameters such as the interaction between temperature and the  $\phi$  value, the sensitivity factor is negative, showing that the reactor is not sensitive to the interaction between temperature and  $\phi$  value. Also, for interaction between  $P$  and  $\phi$ , for a range of pressure (17-31 bar), the sensitivity is negative as well showing that pressuring the reactor has no effect on the target parameter. In light of the above discussion, using the thermochemical equilibrium analysis and the RSM model, the optimised operating condition of the proposed process was estimated and represented in Table 3:



**Fig. 14.** Interaction analysis plot for the operating conditions of reactor R<sub>2</sub>.

**Table 3.** The optimised operating conditions obtained for reactor R<sub>2</sub>.

Parameter	Value	unit
<b>Reactor R<sub>1</sub>*</b>		
Temperature	373	K
Pressure	1	Bar
Nitrogen/Ga ratio	0.5	[ ]
<b>Reactor R<sub>2</sub>**</b>		
<i>Target parameter (ammonia is maximised):</i>		
Temperature	373	K
Pressure	5	Bar
Steam/GaN	1	[ ]
<i>Target parameter (hydrogen is maximised)</i>		
Temperature	673	K
Pressure	1	Bar
Steam/GaN ratio	0.95	[ ]
<b>Reactor R<sub>3</sub>***</b>		
Temperature	5000	K
Pressure	1	Bar

\*Kiln reactor, \*\*Fluidised bed reactor, \*\*\*Plasma reactor.

#### 4. Advantages, potential challenges and future works

The proposed process offers the following advantages in comparison with the current pathways for hydrogen and ammonia production:

- 1) ***Zero carbon process:*** The proposed process takes advantage of nitrogen fixation and does not involve any carbon-containing components, hydrogasification, partial oxidation of carbonaceous feedstock, water-gas shift, Boudouard and methanation reaction, which in turn offers a CO<sub>2</sub>-neutral process for the production of clean fuels.
- 2) ***Sustainability:*** Thanks to the plasma reactor, the developed process offers a sustainable chain (loop) of chemical reactions from gallium to gallium nitride (via kiln reactor), gallium nitride to gallium oxide (via fluidised bed reactor) and gallium oxide to gallium (via plasma reactor). Reactors R<sub>1</sub> and R<sub>2</sub> are commercially available and the knowledge of handling gallium at T~673 K has already been developed. The products of the process are oxygen and hydrogen which are environmentally benign. For ammonia, the knowledge of handling and storage has already been developed. Considering the fact that the thermo-equilibrium chemical conversion of the reactors can reach the completion point, it can be stated that the theoretical limit for the chemical conversion extent of the reactors is the highest.
- 3) ***Flexibility in type of the clean fuel product:*** The system offers great flexibility in terms of the final products such that depending on the end-user requirements, the final product can be hydrogen, ammonia or a combination of both, which easily can be separated using a low-temperature condenser. Oxygen is also available as a side product, which can be dispatched to the market.

To harness the proposed process, the following challenges require further investigation:

- 1) ***Robust kiln reactor to handle liquid metals:*** Containing gallium in a kiln reactor at low-temperature operation is feasible through installing liners and cathode protection of the surface. However, such implementations can, in turn, induce a thermal resistance between the walls of the kiln reactor and the liquid metal. This decreases the thermal efficiency of the reactor. Therefore, a thorough assessment is highly recommended to evaluate the performance of the kiln reactor equipped with liner.
- 2) ***Robust nitrogen gas and steam injection technology for the reactors:*** A high-fidelity gas injection system is required for the kiln reactor to avoid agglomeration of GaN particles, while uniformly distributes the nitrogen gas in the reactor. Also, a robust

1 steam injection system is required for the fluidised bed to maintain the fluidisation,  
2 heat and mass transfer rate.

- 3 3) ***Kinetic of the reactions in the plasma reactor:*** The proposed system requires a novel  
4 type of plasma reactor fortified with nano-catalyst, which to the best of author's  
5 knowledge has not been developed yet. Hence, there is a lack of information on the  
6 design, configuration and performance of the reactor together with the lack of study  
7 on the kinetics of the gallium oxide dissociation in the plasma reactor.

## 9 5. Conclusion

10 In the present work, we reported the results of thermochemical equilibrium analysis to assess  
11 the feasibility and the thermodynamic potential of a novel process for co-production of  
12 hydrogen and ammonia using liquid metal and a plasma reactor. The process takes advantage  
13 of nitrogen fixation reaction, while offering a sustainable process, which eliminates the  
14 production of greenhouse gases. Thermochemical equilibrium and response surface  
15 methodology analysis showed that the process is thermodynamically feasible. Some of the  
16 advantages and main challenges were identified and the following conclusions were drawn:

- 17 • Within the identified operating conditions, the Gibbs free energy of the reactions in all  
18 reactors was negative showing that the reactions are spontaneous and feasible in the  
19 reactors. In reactors  $R_1$  and  $R_2$ , the enthalpy of the reaction was negative, hence, the  
20 thermal energy released in the reactor can maintain the temperature and also be  
21 partially used to preheat the products before introducing to the plasma reactor. This  
22 can plausibly reduce the energy requirement of the plasma reactor.
- 23 • Thermodynamic assessment showed that the reactor  $R_2$  can be used for the co-  
24 production of hydrogen and ammonia providing that the temperature, and feed ratio of  
25 the reactor ( $\varphi$ ) is regulated such that  $373\text{ K} < T < 673\text{ K}$ ,  $P=1\text{ bar}$  and  $0.1 < \varphi < 1.0$ .
- 26 • The plasma reactor was found to be a plausible configuration to drive the dissociation  
27 reaction of  $\text{Ga}_2\text{O}_3$ , for which  $\Delta G$  is highly positive. This reactor completes the circle  
28 of the reactions without emitting any greenhouse gases and environmental pollutants,  
29 which bring sustainability features to the process.
- 30 • Increasing the steam content in reactor  $R_2$  can harm the quality of the product by  
31 producing  $\text{GaOOH}$  instead of  $\text{Ga}_2\text{O}_3$ , which in turn decreases the mole fraction of  
32 gallium in the outlet of the plasma reactor.

- The response surface analysis showed that apart from temperature, pressure and feed ratio of the reactor, the interaction between temperature and pressure can also affect the performance of reactor R<sub>2</sub>. Hence, a multi-response optimisation, conducted over the RSM model and the optimum operating conditions for the reactor, was identified.

Overall, the proposed process showed a great thermodynamic potential to be used for the nitrogen fixation and production of hydrogen and ammonia. However, a techno-economic assessment together with an energetic assessment of the reactors are highly recommended to be conducted to amend the conceptual design and identify the most suitable configuration and design.

### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### **Acknowledgements**

M. M. Sarafraz acknowledges the support provided by the University of Warwick and University of Adelaide for using software packages. N. N. Tran acknowledges a start-up fund provided by the University of Adelaide. M. M. Sarafraz, N. Pourali, E. Rebrov and V. Hessel acknowledge support from the ERC Grant Surface-Confined fast-modulated Plasma for process and Energy intensification (SCOPE) from the European Commission with the grant number 810182.

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