Nitric acid is one of the most basic and important products of inorganic chemistry. Its worldwide annual production is estimated at the level of 60 million tons (in 2016) with over 50% of this product being used in fertilizers production. Practically all the industrial scale production of nitric acid is via the Ostwald process that is based on ammonia oxidation. Yet to synthesize ammonia in the Haber-Bosch process, hydrogen is a necessity. 70% of this hydrogen demand is assured by methane steam reforming. The Haber-Bosch process is one of the most crucial technologies in human civilization allowing for a constant increase in our population. Its scale is so tremendous that it attributes 5% of the total global consumption of natural gas and 2-3% of global energy demand. In other words, while only part of Haber-Bosch-derived ammonia is used to produce nitric acid, its formation requires a great amount of natural gas. This creates a threat of strong dependence on natural gas resources. Moreover, the conversion of this natural gas produces significant emissions of carbon dioxide. A lot of effort is given to make this fossil fuels-dependent process more sustainable by matching it with green hydrogen and renewable energy [9,10]. However, in the case of nitric acid, it seems that its production can be separated from the ammonia industry. The solution would be plasma technologies. In fact, the very beginnings of nitrogen fixation (via NO formation) roots in air plasma processing in the Birkeland Eyde process. While the process occurred to be much less effective than the Haber-Bosch process, and replace by it in the 1920s, the present ecological awareness, natural gas market, and great improvement in plasma techniques can turn the tables.

The recent research on plasma application in NO_x (sum of NO and NO_2) formation suggests that the most effective of all plasma types is atmospheric pressure microwave plasma (APMP). This high efficiency is attributed to the high temperature of plasma (up to 5000-6000 K) and the presence of vibrationally excited molecules. In the case of air or oxygen-nitrogen plasma, both of these compounds can get vibrationally excited. As a result, they have much higher energy (received via collision with plasma electrons) than in the ground state and can lower the activation energy of NO formation. In fact, these vibrationally excited molecules, especially nitrogen, are often indicated as responsible for the good result of APMW in the context of NO_x production. Whatsmore, APMP reactors are composed of technologically mature components (power supplies, MW magnetrons, waveguides) that are manufactured by many companies. The reactors can work with a high gas output and power input – which creates the possibility of scaling up the technology. Most importantly, plasma reactors affect the gas directly and therefore are characterized by instant on/off procedure. That seems to fit perfectly we time-depended renewable energy sources like solar or wind energy. In other words, applying APMP sourced with renewable energy and air or O_2-N_2 mixtures seems like a promising technology that could replace the traditional Haber-Bosch/Ostwaold process reducing the dependence on natural gas and significantly limiting CO_2 emissions.

However, recent research shows that the APMP process is still far from its energy efficiency optimum. Moreover, the role of vibrationally excited molecules in the process is still not fully understood and proven. Therefore, the goal of this project is to apply and investigate quenching as a possible way of improving process efficiency. This will be obtained by introducing de Laval nozzle and additional cooling gas. The nozzle changes the thermal energy into kinetic one, cooling the gas and enhancing heat transfer. This should provide a very fast cooling rate (quenching). As a result, a higher yield of NO_x should be possible to obtain. Without quenching, high shares of NO_x are lost due to reversible rations that lead to the recreation of oxygen and nitrogen. The experiments will be done in a 3 kW APMP reactor with high gas flow rates (up to 100 L/min) for different nitrogen-oxygen concentrations. The experimental results will be supported with an advanced 3D numerical model. Validated by the experimental result, the model will be used to optimize quenching and evaluate the role of vibrational excitation in NO_x formation.

The result of the project will be beneficial in many areas where microwave plasma processing of gases is applied. However, the main goal is to better understand and develop a process that might be crucial for a more sustainable society.