



NET-ZERO INDUSTRIES

MISSION



Project Title

Comprehensive Utilization of Industrial Exhaust Gas to Yield High-Valued Chemicals

Industry Partner

Tianjin University

Industry Sector

Cross Sector

Technology Pathway (Primary)

Materials Efficiency and Industrial Symbiosis

NIM Pillar

Technology Demonstration

Source

NIM Awards 2023

Description

China possesses large amount of industrial exhaust gas rich in CO, such as Linz-Donawitz process gas, yellow phosphorus tail gas, calcium carbide furnace tail gas, arc furnace tail gas, waste gas and other traditional means used as fuel to provide heat, which will bring a lot of carbon dioxide emissions. Taking converter gas as an example, China's annual converter gas generates about 85 billion cubic meters, according to the CO content of 60% calculation, all as a fuel being equal to annual carbon dioxide emissions of about 100 million tons.

This project utilizes the above-mentioned industrial exhaust gas to obtain CO or syngas after purification, and then converts it to produce high-valued chemicals such as ethylene glycol, oxalic acid, calcium formate, dimethyl carbonate, ethanol and etc, so as to achieve carbon fixation and high-valued utilization of exhaust gas. Relevant technologies have been authorized 7 international invention patents in the United States, Europe and other countries, and 32 Chinese invention patents, and they have been industrialized and commercially promoted in China.

A total of 16 industrial tail gas purification equipment contracts have been signed in China, with a total production of 1 million tons/year of ethylene glycol, 50,000 tons/year of oxalic acid, 200,000 tons/year of formic acid, 100,000 tons/year of dimethyl carbonate and 15,000 tons/year of calcium formate. The cumulative annual emission reduction of carbon dioxide is 1.5 million tons.

Innovations Employed

1. A large amount reduction of carbon dioxide annual emission due to the avoiding the direct combustion of industrial exhaust gas to produce carbon dioxide: Comprehensive utilization of industrial exhaust gas to yield high-valued chemicals was realizes in industries. A total production of 1 million tons/year of ethylene glycol, 50,000 tons/year of oxalic acid, 200,000 tons/year of formic acid, 100,000 tons/year of dimethyl carbonate and 15,000 tons/year of calcium formate. The cumulative annual emission reduction of carbon dioxide is 1.5 million tons.
2. Industrial exhaust gas purification and CO separation and purification technology: An adsorbent with high adsorption capacity and high selectivity for CO and complete sets of CO pressure swing adsorption were invented; A complete set of key technologies for continuous catalytic oxidation purification of yellow phosphorus tail gas and CO purification was invented; A complete set of key technologies for deep purification of complex components of calcium carbide furnace tail gas and CO purification were invented.



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3. Key technology for the synthesis of catalysts for oxalic acid production by CO carbonylation and diversification of its downstream derivatives: Invention of Pd catalysts for oxalate synthesis and key technologies for their preparation; Invention of a coupling-regeneration steady-state closed self-cycling clean production process for oxalic acid production by CO and development of diversified high-value-added product solutions.
4. Key technology for the synthesis of a series of Cu-based catalyst for ester hydrogenation: Invention of high stability Cu-based catalyst for oxalate hydrogenation to ethylene glycol and its preparation technology; Invention of high activity Cu-based catalyst for methyl acetate low temperature hydrogenation and its preparation technology; Invention of Cu-based catalysts with high selectivity and low hydrogen-ester ratio for the hydrogenation of vinyl carbonate to methanol and its preparation technology.

Dimension of Novelty

Company & Country

It was new to Company, Country and International

Innovation Collaboration

In-house

n/a

Cooperation with scientific institutions

n/a

External Partners

External collaboration: Tianjin University and Peking University Pioneer Technology Co., Ltd., Shandong Acid Technology Co., LTD., Dalian Reak Science & Technology Co., Ltd.

Intellectual Properties

Patents: 32 Chinese patents and 7 international patents have been authorized in the comprehensive utilization of industrial exhaust gas.

IP Links

Not Found

Timetable & Progress

System complete and qualified. First of a kind commercial system (TRL 8):

The comprehensive utilization of industrial exhaust gas to yield high-valued products such as ethylene glycol, oxalic acid, formic acid, calcium formate and dimethyl carbonate are all first commercialized in China.

Project started 2010:

Related technologies began to be developed in 2010s, including industrial exhaust gas purification and CO purification by pressure swing adsorption technology, preparation of ethylene glycol, oxalic acid technology by syngas, calcium hydroxide carbonylation synthesis of calcium formate, methanol oxidation carbonylation synthesis of dimethyl carbonate, preparation of ethanol by syngas, etc., are all scaled up from the laboratory through pilot testing and eventually industrialized.

Financing (Public/Private)

Funding Public - Yes

The research and development process was supported by projects related to China's National research program and also the financial support from enterprises.



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Finance Links	National Research Program - China
Project Phase TRL	TRL 8
Problems to be Solved and Risks to be Managed	Through joint research and development, this project has solved the problem of high cost and low efficiency of separating CO from N ₂ and CH ₄ , and developed continuous, stable and efficient purification technologies such as desulfurization, denitrification and dephosphorization for different industrial exhaust gases. It has solved the difficulties of easy flying temperature of catalyst bed and diffusion limitation during the carbonylation reaction process of series products, and the problems of sintering-induced deactivation and high hydrogen-ester ratio required for Cu species of hydrogenation catalysts under high temperature hydrogen-rich reaction conditions. The process risk of this project is mainly the removal of impurities from complex industrial exhaust and their impact on the catalytic reaction, which has been solved by the reaction/adsorption means and the improvement of the catalyst anti-toxicity.
Preliminary or Final Results Achieved	This project has created a new mode of resource utilization of CO-containing industrial exhaust, breaking the technological monopoly of Japan and other foreign countries. At present, it has been successfully promoted and applied to 22 sets of industrial production equipment of oxalic acid, ethylene glycol, dimethyl carbonate and other oxygen-containing chemicals made from steel mill exhaust, yellow phosphorus tail gas, calcium carbide tail gas, semi-coal tail gas, etc which has added ¥3.619 billion yuan of new sales revenues in the past three years, and ¥1.135 billion yuan of new profits, and formed the diversified and high added-valued bulk oxygen-containing compounds product chain, and at the same time, reduced the CO ₂ generated from the combustion of its emissions, and made significant contributions to the promotion of resourceful and high value utilization of industrial exhaust gas, emission reduction and efficiency enhancement of enterprises, technological innovation and diversified and differentiated development, with remarkable economic and social benefits. The research about this project has gained Chemical Society of China Basic research First prize, China Petrochemical Federation Technical research First prize, China Patent Excellence Award and Tianjin Patent Award.
CO₂ Emissions Reduction Potential - Implementation and Future Market	Industrial tail gas purification technology has been popularized and applied to steel mill tail gas, calcium carbide furnace tail gas, yellow phosphorus tail gas and semi-coal tail gas as raw materials, and a total of 16 industrial tail gas purification equipment contracts have been signed in China, with a total production of 1 million tons/year of ethylene glycol, 50,000 tons/year of oxalic acid, 200,000 tons/year of formic acid, 100,000 tons/year of dimethyl carbonate and 15,000 tons/year of calcium formate. The cumulative annual emission reduction of carbon dioxide is 1.5 million tons.
Market Positioning	Industrial exhaust gas purification technology has been promoted and applied to steel mill tail gas, calcium carbide furnace tail gas, yellow phosphorus tail gas and semi-coal tail gas as raw materials and a total of 16 industrial tail gas purification equipment contracts have been signed, with a market share of more than 50%.



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Applying the converter tail gas purification and CO purification technology of the steel mill, the ethylene glycol production capacity of Shanxi Woenergy Chemical Industrial Technology Co., Ltd. has reached the designed full load of 300,000 tons/year after being put into operation in August 2020; Applying the converter tail gas purification and CO purification technology of the steel mill, as well as Tianjin University's oxalic acid production through CO hydrolysis and crystallization complete set of technology and synthesis of oxalic acid through methanol carbonyl hydrolysis technology, Shandong Acid Technology CO., Ltd. built equipment with 50,000 tons/year oxalic acid, 200,000 tons/year formic acid production in September 2018. Tianjin University and Dalian Reak Science & Technology Co., Ltd. produced and sold a total of 871.777 tons of ester hydrogenation Cu- based catalysts, with a market share of 30%. In summary, if only the economic benefits of the representative application units in applying this technology from year 2019 to 2022 are calculated, the total new sales revenue will amount to ¥3.62 billion yuan and the new profit will amount to ¥1.13 billion yuan. If the economic benefits of the above units since the application of the technology are calculated, the new sales revenue will amount to ¥4.35 billion yuan, and the annual output value will exceed ¥8 billion yuan.

Project Location

China

Project & Technology Links

Patents, pdf, Certificate of International and Chinese patents.

Pictures and Certification, pdf, The picture about the demonstration applied into industries and the corresponding certification of the technologies applied in the industries.

Technology Links

Not Found