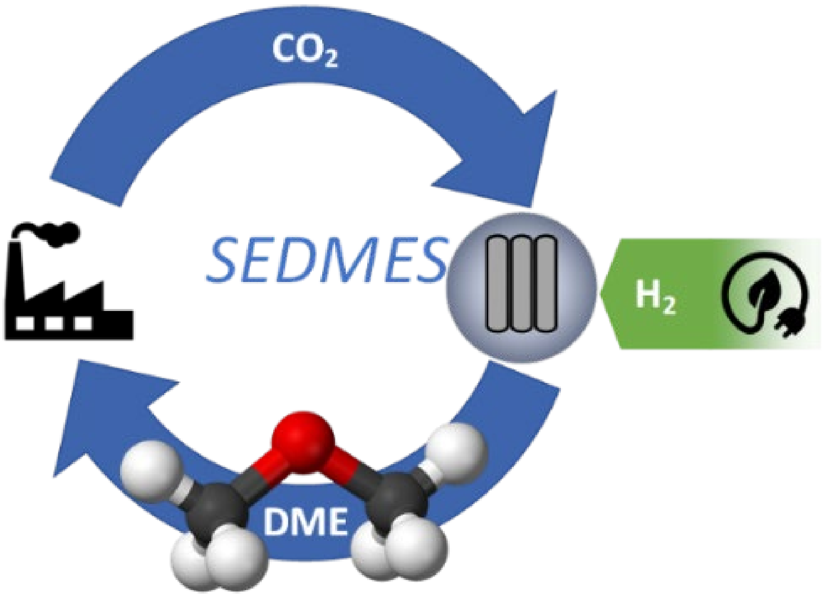
iDME -*I*ndustrial *DME* via Sorption-

Enhanced DME Synthesis (SEDMES)- iDME

Public report



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iDME

*I*ndustrial *DME* via Sorption-Enhanced DME Synthesis (SEDMES) – Public report

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Contents

Samenvatting

Om klimaatverandering tegen te gaan, moet de Nederlandse industrie tegen 2050 klimaatneutraliteit bereiken, wat aanzienlijke emissiereducties vereist tegen 2030. Koolstofafvang, -gebruik en -opslag (CCUS) technologieën zijn cruciaal om deze doelen te behalen, en nieuwe processen zoals Sorption Enhanced DME Synthesis (SEDMES) worden ontwikkeld om deze transitie te bewerkstelligen.

SEDMES, ontwikkeld door TNO, is een proces dat de omzetting van CO_2 naar dimethylether (DME) met hoge procesefficiëntie, mogelijk maakt door de *in situ* verwijdering van stoom met behulp van een vast adsorbens. In het iDME-project is deze technologie verder ontwikkeld en bestudeerd voor het hergebruiken van koolstofrijke restgassen uit aardgas, biomassavergassing en staalproductie zonder voorafgaande koolstofafvangst.

De toepassing van SEDMES in verschillende use cases in de staal-, olie- en gas- en biogebaseerde industrie zijn onderzocht door middel van simulaties, samen met de relevante operationele parameters. Belangrijke algemene bevindingen zijn onder meer dat verhoogde druk de productiviteit en selectiviteit verbetert, evenals verhoogde H_2-koolstof ratio's. Verhoogde debieten verlagen juist de selectiviteit. Bij de simulaties met industriële lijken de prestaties ook te verbeteren bij toenemende druk in de aanwezigheid van andere (inerte) gassen, zij het lineair.

Voordat de technologie werd gedemonstreerd in de eerder door TNO ontwikkelde pilootinstallatie, is de chemische stabiliteit van de katalysatoren op laboratoriumschaal bevestigd onder normale SEDMES-omstandigheden. Alleen hoge stoomblootstelling, buiten de normale SEDMES-condities, veroorzaakte omkeerbare veranderingen in de γ-Al_2O_3 katalysator. Grondige analyse van de experimentele laboratoriumresultaten leidde daarnaast tot het inzicht dat een langdurige purge de SEDMES prestaties kan verbeteren door de 3A zeoliet beter te drogen.

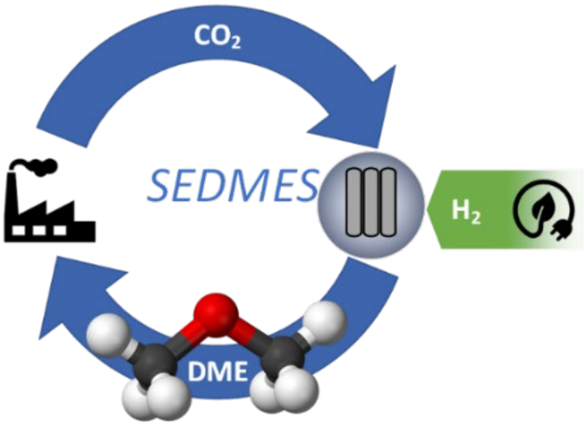
De resultaten van lange duur experimenten op pilotschaal (40 bar) bevestigde de goede prestaties bij hoge druk. Desalniettemin, waren de prestaties minder dan voorspeld met het model, wat toegeschreven kan worden aan de regeneratie van het adsorbens, die verbeterd moet worden.

De belangrijkste bevinding uit de techno-economische analyses is dat de economische haalbaarheid afhangt van de kosten van waterstof. Dit benadrukt het belang van de purge loop die binnen het project werd ontwikkeld. Deze purge loop voor het recyclen van waterstof werd ontworpen en gebouwd binnen het project, maar helaas nog niet volledig getest. Toekomstige kostendalingen in de productie van groene waterstof zullen naar verwachting SEDMES economisch aantrekkelijk maken. Voor de olie- en gasindustrie bleek het direct omzetten van CO_2-bevattend aardgas naar DME minder efficiënt en kostbaarder dan het afvangen van CO_2 voorafgaand aan gebruik in de onderzochte gevallen. Voor de staalindustrie bleek de toepassing van SEDMES een zeer interessante optie voor verdere ontwikkeling.

Het iDME-project heeft het potentieel van SEDMES-technologie gedemonstreerd voor efficiënt en kosteneffectief hergebruik van industriële restgassen, wat bijdraagt aan het doel van klimaatneutraliteit in 2050. Verder onderzoek en ontwikkeling, met name in het optimaliseren van waterstofefficiëntie en optimalisatie van de integratie van SEDMES inclusief de downstream zuivering, zullen essentieel zijn voor volledige implementatie van de technologie op grote schaal.

1 Project information

Project titel	Industrial DME via Sorption-Enhanced DME Synthesis (SEDMES) -IDME
Project number	060.50391
Coordinator	TNO
Project period	01-04-2022- 31-03-2024
RVO Program line	MMIP 6 - Sluiting van industriële ketens



This work has received funding from Topsector Energie of the Ministry of Economic Affairs and Climate Policy (TIND121010).

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Organisation	**location**	**Main contact**	**e-mail**
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2 Background and objectives

2.1 Introduction

To combat climate change, industrial processes, products and feedstock need to become climate neutral, and industrial cycles have to be closed by 2050. Already a great deal is required from the Dutch industry to achieve the targeted emission reductions of 19.4 Mton CO_2 by 2030. Carbon capture, utilisation and storage (CCUS) technology can enable the industry to achieve the short term 2030 targets while continuing to build an industry that can be circular in 2050. Reuse of carbon-rich industrial residual gases (CO/CO_2) supports the transition towards the circular use of raw materials, provided the energy input comes from renewable electricity, green hydrogen. Novel processes need to be developed for the effective and efficient reuse of residual gases. Sorption enhanced DME synthesis (SEDMES) is such a novel process developed by TNO. It comprises in situ steam removal with a solid adsorbent, ensures high CO_2 conversion efficiency to DME in a single unit operation. The in situ removal of steam, shifting the equilibrium to the product side, has been shown to enhance catalyst lifetime and boost process efficiency, specifically in the case of diluted CO_2-rich gas streams.

2.1.1 Sorption enhanced DME synthesis (SEDMES)

Separation enhanced synthesis routes have shown to offer major advantages in the conversion of carbon dioxide to chemicals including DME1[i]. In fact, SEDMES has proven to yield a very high carbon selectivity to DME. SEDMES is a reactive process, in which steam is removed in situ by using a sorbent. As a typical pressure-swing-adsorption (PSA) system, it undergoes a cycle of reactive adsorption and sorbent regeneration, as illustrated in Figure 1. A typical SEDMES cycle consists of at least the following four consecutive steps:

i) Adsorption (ADS) – the feed is converted into DME on the catalyst, while steam is removed by a zeolite adsorbent;
ii) Blowdown (BD) – counter-current depressurisation of the system in order to desorb water;
iii) Purge (PURGE) – counter-current flow of dry hydrogen to remove water from the column;
iv) (REP) repressurisation – co-current pressurisation of the column with the feed stream.

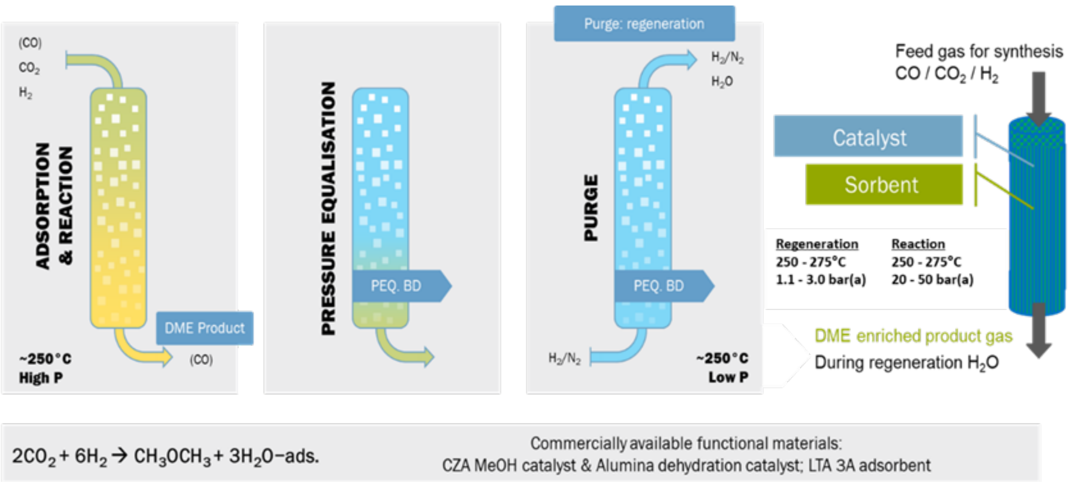

Figure 1: SEDMES cycle with the consecutive steps adsorption (ADS); Blowdown (BD); PURGE and repressurisation (REP).

The SEDMES technology has been successfully brought from lab to pilot scale (3 kg/h), making use of existing infrastructure of other sorption enhanced processes. In iDME the dedicated SEDMES facility was employed (Figure 2) to scale-up and further develop the technology.

Figure 2: SEDMES pilot in Petten.

2.2 Project objectives & structure

The objective of iDME is to establish a benchmark for energy and cost efficient reuse of residual gases from three industrial sources: natural gas, biomass gasification, and steel-making. The development of the SEDMES technology, will enable the much-anticipated role of DME as an industrial fuel and platform chemical. As such it provides an essential element in closing industrial cycles.
The project aimed at an optimised industrial DME production process, which includes a cycle design for SEDMES and extensive experimental validation of sorption-enhanced production of DME from CO_2, for 3 industrial use cases: (1) (bio-based) CO_2-containing flue gas, (2) blast furnace gas, and (3) captured CO_2.

The workplan of the iDME project was divided into 4 work packages, ranging from investigating the material chemical stability under the relevant conditions (WP1), SEDMES modelling and cycle design (WP2), experimental validation (WP3) to the economic perspective of the iDME concept (WP4). Furthermore, a purge loop was designed and built within the project to recycle the hydrogen that is used for the purge, making the overall process more efficient and less expensive as H_2 is the main cost driver.

3 Results of the project

3.1.1 WP1 Enabling research

The objective of this work package was to investigate the chemical stability of the materials. Specifically mapping of catalyst deactivation under relevant, sorption-enhanced, conditions (temperature and steam partial pressure) was unknown and therefore was necessary to be investigated before the testing in the pilot installation. To this end, cyclic experiments (up to 100 cycles per setting) were conducted at various temperature and steam contents in the lab.

No degradation was observed in the normal SEDMES operation range. More extreme temperatures and especially exposure to high steam contents led to reversible changes in the γ-Al_2O_3 catalyst: coverage Lewis acid site by adsorbed water. Furthermore, it was found that long duration purging can increase SEDMES performance caused by better 3A zeolite drying.

3.1.2 WP2 Modelling and process design

To analyse the SEDMES process and optimise its operation a dynamic reactor model was developed at TNO previously[ii]. Four use cases were formulated in different industries): i) Steel industry, ii) Oil&gas industry and iii) Biomass gasification. These cases were investigated by simulations and their business case study is described in 3.1.4 WP4 Business case and roadmap.

The SEDMES performance for the experimental campaigns with the pilot in WP3 (only CO_2 and H_2 feed) and the cases was evaluated by finding the maximum productivity of each mixture with the following variables: i) Pressure, ii) Cycle time, iii) Flow rates and iv) hydrogen-carbon ration known as M-module: $(H_2\text{-}CO_2)/(CO+CO_2)$. This was achieved by changing the duration of each step of the cycle while keeping the ratio of step time over total cycle time constant to ensure continuous operation.

The overall conclusion from the modelling efforts is that the optimum operation point of SEDMES depends heavily on the application, but several trends became apparent. First, increasing pressure greatly increases both productivity and selectivity (Figure 3). This increase is significant going from 20 to 30 bar, but less so when increasing further to 40 bar. A drawback of operation at higher pressure is the increased DME loss via the blowdown. Thus, ultimately also here an optimum will depend on the use case. Second, increasing the M-module increases productivity and selectivity. Third, increasing the flow greatly decreases selectivity. Lastly, the presence of CO is advantageous in terms of productivity.

The effect of inert presence to the SEDMES process was assessed to study the capability of using industrial waste streams as a feed (Figure 3). In case of biomass gasification feed, there will be high presence of methane in the feed. This composition of ~65 wt% CH_4 was selected to illustrate the use of a diluted carbon feed stream. As can be seen in Figure 3, the gasified biomass composition (red colour) results in lower selectivity and lower productivity than the H_2 and CO_2 only feed. However, the results show that it is possible to operate SEDMES under such conditions. The same trend of increasing performance by increasing pressure is noticed, but this time the pressure increase linearly improves performance of both selectivity and productivity. In contrary, the positive effect of pressure increase is more profound in lower pressures than in the non-diluted case. The next step would be to also include modelling of the purification is necessary, combined with an elaborate techno-economic evaluation to define optimum operating conditions per use case.

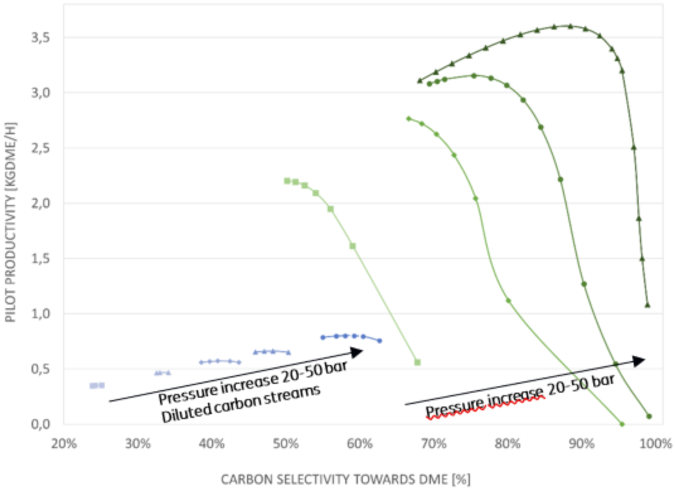

Figure 3: Pareto plots showing the SEDMES productivity-selectivity trade-off as a function of the pressure, with (red) and without (green) inert gases.

3.1.3 WP3 Experimental campaign

A critical step to enable implementation of industrial DME production via sorption-enhanced DME synthesis is to establish confidence in the feasibility and reliability of the technology for industrial applications. The confidence in long-term operation and stability will be established by continuous duration testing. The duration experiments were conducted on the previously developed pilot installation in Petten shown above.

Figure 4: Purge Loop skid. Right: hoisted into the SEDMES container in Petten.

To improve the SEDMES pilot and make it more efficient a recycle loop for the purge stream was designed and built within the project. This purge loop has the purpose of separating H_2 from water in order for the H_2 to be reused for purging in a subsequent cycle and thus reducing the H_2 requirements and thus costs. The full skid was assembled and tested in house at TechnipFMC before being transported to TNO where it has been incorporated in the SEDMES pilot (Figure 4). Unfortunately, significant challenges during this activity were encountered: i) frequent design changes as the operations progressed and ii) long procurement times. Therefore, this was only realised at the end of the project and no resources were available to run the pilot with the purge loop. This will be part of a follow-up project.

The iDME duration testing marked the first experimental campaigns with the SEDMES pilot at higher pressures (40 bar). These unprecedented pressures led to unforeseen issues:

- Hydrogen leakages. Hydrogen is a very light gas and caused several leakages that had to be solved.
- Attrition of the sorbent material caused high pressure drops in the system. This was not observed in previous projects on smaller scale installations. Therefore, adjustments needed to be made to the reactor.

The latter was an important and unforeseen finding in the scale-up of the SEDMES development and prompted us to start discussions with the sorbent provider and switch to a different and stronger type of sorbent material in the future.

After solving these issues, the SEDMES pilot was operated for over 300 hours. Similar to model predictions, both the DME selectivity and productivity notably increase at higher pressure. However, the results with the pilot do not reach the predicted values. This deviation can be attributed to reduced water adsorption: A key aspect of SEDMES is the purge step in which the sorbent is regenerated to be ready to adsorb steam in the subsequent cycle. If the zeolite is not completely dry, the enhancement capacity in the next cycle is less and it can be accumulated over cycles. This fact might be causing a low performance in the SEDMES pilot and will be investigated in follow-up projects (e.g. POWERED).

3.1.4 WP4 Business case and roadmap

In WP4 the business case for the formulated cases in the steel and oil and gas industry was investigated and a roadmap for SEDMES development in these sectors was developed. The transformation of CO_2 to DME represents a promising opportunity for the oil and gas industry to reduce carbon emissions while creating value-added products. For both industries a case with and a case without CO_2 capture were studied and compared.

The techno-economics of the SEDMES process incorporated in the processes described above was assessed, both by a group of PDEng students from the university of Eindhoven and by Technip FMC an TataSteel. In all cases the main finding is that the economic viability hinges on the cost of hydrogen, which is a key input for the reaction. Currently, the cost of green hydrogen produced from renewable sources is higher than grey hydrogen that is produced from fossil fuels. However, as the technology for green hydrogen production advances and scales up, the cost is expected to decrease which will make SEDMES more attractive. One of the outcomes of the technoeconomic analysis of the SEDMES project for oil and gas case is that SEDMES could become economically viable when the cost of green hydrogen drops below the current grey hydrogen price. Another outcome is that converting CO_2-containing natural gas directly to DME would results in lower CO_2 conversion efficiency and higher cost of producing DME compared to a process where CO_2 would be first removed from natural gas and then converted to DME. In the steel case using SEDMES for carbon tuning within the process still holds as an interesting case as DME can be used in a number of ways related to the ironmaking process, such as hydrogen storage and as fuel additive. The integration of SEDMES in the steel making process is being patented by TataSteel and will be studied further in the POWERED project.

4 Bottlenecks and follow-up

During the iDME project some challenges were encountered which are described below. Despite these challenges the iDME project has achieved most of its' deliverables and goals and has led to key insights for the further development and upcaling of the SEDMES technology.

4.1 Bottlenecks

Technical & Operational challenges

The following technical and operational issues were encountered during the project:

- H_2 leakages in the pilot
- Mechanical attrition of the sorbent material
- The design and incorporation in the SEDMES process was more challenging than anticipated with more frequent design changes than Technip FMC is used to (being an R&D installation) and ii) long procurement times.

The complexities faced impacted the project's timeline and an extension of 3 months was approved by RVO.

4.2 Follow-up of the iDME project

During the course of the iDME project already two follow-up projects were secured in which the SEDMES technology will be advanced further:

- MOOI22 POWERED project: The goal of the POWERED project is to pilot the SEDMES technology at the Energy Transition Campus Amsterdam and prepare a first commercial demonstration in a follow-up project led by industry partners. Furthermore, the project investigates the ability of the process to cope with the intermittent nature of renewable electricity and minimise the costs by a smart energy management system (EMS).
- HEU BUTTERFLY project: BUTTERFLY – Biomass Utilized To The Extended portfolio of Renewable Fuels with Large Yields - is an Horizon Europe Innovation Action project that aims to develop innovative and flexible co-production of renewable & recycled carbon DiMethyl Ether (rDME) and Synthetic Natural Gas (SNG) from waste and residual feedstocks, targeting the off-grid energy supply, the steel industry and heavy transportation. It will demonstrate the SEDMES technology downstream an indirect biomass gasifier at TRL 7 in France.

5 Contribution to objectives of the program

The iDME project is specifically contributed to MMIP6, the utilisation of residual carbon streams. In addition, there is a strong connection to MMIP 8, the application of renewable H_2 in chemical production processes. SEDMES can make a substantial contribution to the reduction of Dutch CO_2 emissions by 1) reducing the cost and improving the economy for CO_2 (capture and) utilisation in the steel industry, and up- and downstream in the (bio-based) chemical industry, 2) integrating the value chain for the reuse of residual CO_2 in high efficiency industrial DME production, 3) maintaining and advancing the leading Dutch knowledge position. One major advantage is that SEDMES technology can convert the diluted carbon streams, typical for steel gases, but also for other residual CO_2 streams, directly into high-value product DME without requiring a separate carbon capture process. In addition, the industrial DME can be used again in the energy-intensive industry for defossilisation, particularly in high-temperature industrial heating. In the chemical industry the demand for hydrocarbon based chemicals and feedstock is anticipated to remain very large, so bio-based and synthetic alternatives are of great importance. Ethylene is the largest hydrocarbon commodity chemical in the world, with 165 Mt annually. A large part of the ethylene is used to produce polyethylene, the most common used plastic in the world today. For the production, DME is an important intermediate reactant in the methanol-to-olefin process. Hence, the chemical industry can use industrial DME to make sustainable alternatives for their product portfolio.

	Technologische route	Gereedheidsniveau technologie[1]	CO_2 emissies (scope 1) [t/ t ruw staal]	Energieverbruik[2] [GJ/ t ruw staal]	Moeilijkheidsgraad implementatie in primaire route[3]
Huidig	Hoogovens & BOF	11	1.8	17-19	-
BF-CCUS	Hoogovens & BOF **met BF-CCUS**	5	0.4	22-24	
Alternatieve reductie-technologieën	**DRI technologie** o.b.v. aardgas met CCUS	9 (11 excl. CCUS)	0,3[4] 0,6 (Excl. CCUS)	13-15	
	DRI technologie o.b.v. waterstof[5]	5	0,04[6]	11-13	
	Fluidized bed DRI o.b.v. waterstof	4	0,04[6]	11-13	
	Suspension ironmaking technologie	3	0,04[6]	n.b.	
	Plasma directe staalproductie	4	0,04[6]	n.b.	
	Elektrolytische processen	4	0,04[6]	12-14	

Hoog Laag In scope van de haalbaarheidsstudie

1) Gebaseerd op TRL-definities in IEA – Iron and Steel Technology Roadmap (oktober 2020), Bereik van 1 (initiële concept) tot 11 (bewijs van stabiliteit bereikt);
2) Gebaseerd op interviews met experts en EPRS – Carbon-free steel production (april 2021); 3) Inclusief impact integratie in staalproductie proces;
4) Ervan uitgaande dat CO_2 in topgas wordt afgevangen; 5) DRI technologie draait op 100% waterstof; 6) Aangenomen dat het hele proces wordt aangedreven met groene energie

Bron: IEA (oktober 2020), European Parliamentary Research Service (april 2021), Expert Interviews, Roland Berger

Figure 5: Indicative overview of steel production technologies for CO_2 emission reduction.[iii]

In Figure 5 an indicative overview of steel production technologies for CO_2 emission reduction is shown. Carbon capture and utilisation is technically feasible with limited impact for the steel production process, allowing to maintain product mix and quality. As shown in Figure 5 with CCUS already 1.4 ton CO2 emission per ton steel can be mitigated (scope 1). Moreover CCUS technology can achieve Tata Steel's 2030 emission reduction ambitions, in contrast to long-term alternative iron making (DRI with green H2).

Where CO_2 emissions for the Dutch iron and steel industry are about 12 Mt/yr, the total industrial sector still emits around 55 Mt/yr with a large contribution from the chemical industry. To achieve the targeted emission reductions by 2030, still a great deal is required from industrial parties. This stresses the potential of CCUS technology for emission reduction in the Dutch industry. Similar as discussed for the steel industry, CCUS technology can enable the industry to achieve the 2030 targets, in contrast to longer-term alternatives. Within the iDME project, these numbers will be calculated in more detail. Also the hydrogen production and the carbon footprint of electricity production, for both current situation and future scenarios, will be taken into account.

6 Dissemination

At the start and the end of the project a newsflash of the iDME project was launched on LinkedIn.

The iDME results were presented at LPG week (runner up presentation price) and ICCDU 2023 (2 oral presentations).

A review paper[iv] was prepared by TNO in collaboration with partners. Other peer-reviewed publications are pending due to the delays with the pilot and the high IP potential of the findings in the R project. The project resulting in two patents (in preparation): one on SEDMES operation by TNO and one on the incorporation of SEDMES in Steel manufacturing by TataSteel.

7 Signatures

Petten, 28 June 2024

ValidSigned by Sjaak van Loo on 2024-06-29 17:06:15	ValidSigned by Soraya Sluijter on 2024-06-29 20:36:56
S. van Loo Research Manager	S. N. Sluijter Author/ Project manager

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