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# The potential of decarbonising rice and wheat by incorporating carbon capture, utilisation and storage into fertiliser production

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This paper aims to evaluate the reduction in greenhouse gas emissions of rice and wheat and their supply chains by incorporating carbon capture, utilisation and storage into fertiliser production mainly from the ammonia process, which is a part of the fertiliser that produces most of the carbon dioxide. Greenhouse gas emissions of these grains without carbon capture, utilisation and storage are provided from the results of life cycle assessment in the literature. After that, carbon dioxide emission from fertiliser production is quantified. The alternative considered for utilisation is enhanced oil recovery and it is compared with the conventional way of oil production. The effects of carbon capture, utilisation, and storage on greenhouse gas reduction are presented in terms of the supply chains of rice and wheat to make people conscious about the use and optimisation of food. The reduction of greenhouse gas is around 6–7% in the rice supply chain e.g. rice milk, spoons of uncooked rice and 14–16% in the wheat supply chain e.g. pasta, one slice of bread. Although the alternative for carbon dioxide storage demonstrates marginally higher greenhouse gas reduction, enhanced oil recovery may offer an economic incentive from additional oil production that could reduce the cost of rice and wheat.

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### Introduction

Global carbon dioxide (CO2) emissions have continued to rise significantly increasing the potential for catastrophic climate change. In the recent Paris Agreement on climate change established with the Intergovernmental Panel on Climate Change (IPCC), a new goal has been set to limit temperature rise to 2 °C.1 The agricultural sector also contributes to worldwide greenhouse gas (GHG) emissions, 2,3 with a share that is 10-12% of CO<sub>2</sub> equivalent. Considering indirect emissions from other activities related to agriculture such as fertiliser production, land use change, food storage, packaging etc., this share can be up to one-third of the total GHG emissions. 4 It is acknowledged that fertilisers are basically produced from ammonia. Of the total ammonia production in the world, 85% of the product is used to produce fertilisers for growing human and animal food.<sup>5</sup> It then follows that the feedstock used in ammonia production will play a significant role in the amount of energy consumption and CO2 emissions produced during food production.

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It is estimated that ammonia production consumes almost 1.2% of total global primary energy which contributes to 0.93% of GHG emissions.<sup>6</sup> About 70% of the ammonia production in the world is based on steam methane reforming (SMR) technology, and this is mainly because SMR is considered to be the best proven technology which is cost-effective and has low energy consumption.<sup>5</sup> Further reduction of CO<sub>2</sub> emissions to near zero from ammonia production could be only realised by using appropriate CO2 capture, utilisation, and storage (CCUS) technology. As such, this could prove to be a feasible approach to reduce GHG emissions of the fertiliser in food cultivation. Current studies have mainly focused on the gas separating technologies of SMR processes e.g. PSA, TSA or membrane which aim to obtain and recover a high purity product gas.8,9 Thus, during the process, high purity CO2 is generated as a product in the intermedium process. Additional CO<sub>2</sub> is generated by burning additional fossils to increase the temperature in the SMR reactor as well as to generate steam and electricity for use in the process. The industrial sector (including ammonia and fertiliser synthesis) has not received the same attention as power plants for the deployment of carbon capture and storage (CCS) due to its associated costs and no economic incentive. 10 However, there are opportunities for CO<sub>2</sub> utilisation (CU) based on ammonia production because the CO2 concentration in the flue gas is higher than those in other processes e.g. power plants which are usually in

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the range from 4% to 20%.11 Thus CO2 from an ammonia plant at high purity is ready for CU e.g. for enhanced oil recovery (EOR), polymers, urea, CH<sub>4</sub>, methanol, etc.<sup>12</sup> Although CU faces some challenges e.g. low energetic level and reactivity, CU could reduce the cost of capturing additional CO2 and its storage process when compared with that of CCS. 13 Currently, CO2-EOR is considered as an available technology that has been used successfully in North America to increase the oil production from depleted fields. Large amounts of the injected CO<sub>2</sub> could be retained in storage. <sup>14</sup> Most importantly, EOR offers an opportunity where the CO2 can be sold in highvolumes to a customer. In addition, revenue for selling CO<sub>2</sub> could be an incentive to accelerate the deployment of CCS in the industry. However, CU is an energy and material intensive process. Thus, to clarify whether it allows for a net reduction of environmental impacts, every alternative for CO2 utilisation must be evaluated in terms of a life cycle perspective. 15 Another alternative to reduce GHG emissions in food cultivation is the use of organic fertilisers. A number of research studies have investigated this issue in terms of energy use, GHG emissions, and cost-effectiveness when compared with that using conventional fertilisers. 16,17 From a technical perspective, although the environmental impact e.g. aquatic and human toxicity potential, eutrophication and acidification potential is reduced by using organic fertilisers, it makes little contribution to the reduction of global warming potential (GWP). 18 Comparably, a few studies claim that organic food could be better than the conventional food with regard to life cycle assessment (LCA) and the results are much associated with raw material inputs and CO2 emissions. 19,20 Thus, an alternative method is expected to be figured out which could be a good solution to this CO2 issue for the food when compared with organic food.

This paper aims to evaluate the CO<sub>2</sub> emission reduction in rice and wheat by incorporating CCUS into the supply chain via the ammonia plant, which is the main source when CO<sub>2</sub> is regarded to be produced from fertilisers. These grains are selected to be research objects because they provide most of the world's food supply.21 The general technical route is shown in Fig. 1. The GHG emissions of grains without CCUS are compared with those using CO2 storage and utilisation. EOR is selected and analysed as an alternative for CU. Several previous research studies have presented the LCA of rice and wheat. However, they have not considered CCUS for reducing CO<sub>2</sub> emissions that are generated by grain production. Although the information is obtained from LCA studies, only GWP is evaluated. It is worth noting that this study is the first evaluation to quantify the amount of CO2 reduced by incorporating CCUS in fertiliser production which could give more insights and inspirations to the general public. The framework of this paper is illustrated as follows: GHG emissions for the selected grains from different references are presented in section 2. To estimate the overall capture rate of the ammonia plant, technical assessment is then carried out and described in section 3. After that, in the same section, GHG emissions for grains with CCUS are estimated followed by conclusions in section 4.

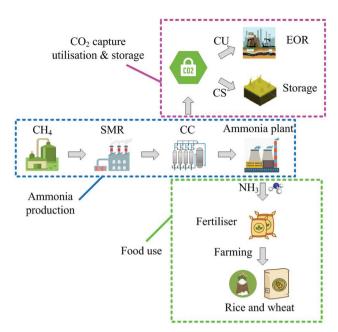


Fig. 1 Alternatives to decarbonised selected food: rice and wheat incorporating CCUS in fertiliser production.

### GWP by selected food

World ammonia (NH<sub>3</sub>) production in 2018 was 176.5 million tonnes per year<sup>22</sup> and represented around 1% of the total world CO<sub>2</sub> emissions. It is predicted to increase to 234 million tonnes per year in 2021.<sup>23</sup> Ammonia production from natural gas using a steam methane process produces around 1.6 tonnes CO2 per tonne NH3 and consumes 28 GJ per tonne NH<sub>3</sub>.<sup>5</sup> This will result in around 374.4 million tonnes of CO<sub>2</sub> per year in 2021. If CCS is incorporated at 90% capture level in all ammonia plants in the world, 336.96 million tonnes of CO<sub>2</sub> per year could be avoided. In this work, rice and wheat are selected to evaluate the reduction of CO2 if CCUS is incorporated. The reason for selecting these crops (rice, wheat) is because they supply most of the world's food<sup>21</sup> and consume a large amount of fertiliser.

Global warming or CO2 equivalent is presented, which is compounded for CO<sub>2</sub>: 1, CO: 2, CH<sub>4</sub>: 21, and N<sub>2</sub>O: 310 according to IPCC.24 The information that comes from different LCA studies is required before estimating the reduction in global warming by incorporating CCUS in selected crop cultivation.

#### **2.1 Rice**

It is extensively acknowledged that rice is regarded as one of the major cereal crops for more than half of the world's population.<sup>25</sup> The cultivation of rice was expected to increase from 510.5 millions of tonnes in 2017 to 565.6 millions of tonnes in 2025.26 This could be mainly attributed to the fact that the demands will increase from 512 millions of tonnes in 2017 to 563.2 millions of tonnes in 2025.26 Its cultivation is one that contributes to the global climate change through emissions of CO<sub>2</sub>, CO, CH<sub>4</sub>, and N<sub>2</sub>O. But at the same time, rice cultivation

and production are sensibly affected by climate change that could not cover the demands in the future.

GHG emissions by rice cultivation in countries from China, the United States, *etc.*, where most of the rice is produced, are presented in Table 1. The GHG depends on location, size of the farms, the variety of rice grains, and yield, among others.<sup>27</sup> The amount of fertiliser used in rice cultivation varies by locations and local farming methods. For instance, in 2014, the amount of fertiliser was 570 kg per hectare in China, 290 kg in Bangladesh, 210 kg in Indonesia, and 130 kg in the United States. It is demonstrated that the variation is mainly because it depends on the fertility of the underlying soil.<sup>28</sup> In Table 1, it can be observed that India and Japan present the highest and lowest emissions, respectively.

#### 2.2 Wheat

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Wheat is the most important crop in the world, which is essential for many human diets.<sup>34</sup> The main countries that export wheat are the United States, Canada, Australia, the European Union, and Argentina.<sup>35</sup> Table 2 presents a global warming impact of wheat cultivation. In 2018, wheat and rice production were 736.1 million and 511.4 million tonnes, respectively.<sup>36</sup> GHG emissions by wheat cultivation and production are lower than those of rice. However, the amount of global wheat production is higher. Therefore, it is important to look for the alternatives to reduce GHG emission in its cultivation.

#### 2.3 CO<sub>2</sub> emissions by fertiliser production in cultivation

Fertiliser production and utilisation is one of the most representative contributors of GWP in rice and wheat production which is successively dominated by CO<sub>2</sub>, N<sub>2</sub>O, and CH<sub>4</sub>. <sup>2,28</sup> For example, the GWP of urea (fertiliser) production and supply in wheat represent around 34%, where 26%, 6.4% and 1.6% are related to CO<sub>2</sub>, N<sub>2</sub>O, and CH<sub>4</sub>, respectively. <sup>28</sup> Table 3 shows the contribution of GHG by fertiliser production in rice and wheat for Bangladesh, Thailand, China, Japan, Sweden, and Australia. Due to the lack of data, one of the assumptions considered in this work is that the percentage of CO<sub>2</sub> generated by fertiliser production only comes from the ammonia process, even when the fertiliser system involves other equipment *e.g.* urea unit after the ammonia plant. The participation of CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> in GHG generated in ammonia production are 91.92%, 7.97%, and 0.11% respectively, according to the

Table 2 GHG emissions of wheat cultivation

Country	System boundary	Unit	Sore	Source
Sweden	Up to-farm gate	kgCO <sub>2 eq</sub> per kg	0.2-0.6	31
Australia	Cradle-to-farm gate	kgCO <sub>2 eq</sub> per tonne	304-487	37
Europe	No specified	kgCO <sub>2 eq</sub> per tonne	381	38
USA	Cradle-to-farm gate	gCO <sub>2 eq</sub> per tonne	356 <sup>a</sup>	39
Iran	Cradle-to-gate	kgCO <sub>2 eq</sub> per tonne	380	40
Poland	Cradle-to-farm gate	kgCO <sub>2 eq</sub> per tonne	364	41

<sup>&</sup>lt;sup>a</sup> An average from nine states from the USA.

Table 3 CO<sub>2</sub> percentage of global warming impact (CO<sub>2</sub> equivalent emission) in some selected countries

Food type	Country	Percentage of GHG by fertiliser production
Paddy rice	Bangladesh Thailand China	$11\%^a$ (ref. 28) $11\%^b$ (ref. 30) $11\%^c$
	Japan	7% (ref. 29)
Wheat	Sweden Australia	24% (ref. 3) 26% (ref. 37)

<sup>&</sup>lt;sup>a</sup> 11% of CO<sub>2</sub> emission by fertiliser production includes manufacture/ transport. <sup>b</sup> 11% of CO<sub>2</sub> emission by fertiliser production includes the input of fertilisers and pesticides, rice seed production and transportation stages. <sup>c</sup> Due to the lack of information, this value is taken from the information provided for Bangladesh and Thailand<sup>28,30</sup> considering that China is located close to these countries.

cradle-to-gate LCA study presented in ref. 42. 91.92% of  ${\rm CO_2}$  is generated by (a) fuel gas combustion in the primary and secondary reformers (93.4%), (b) compressors used to transport natural gas (4.18%), and (c) the steam generation required by the system (2.38%).

## 3. GHG emission assessment of rice and wheat by incorporating CCUS

In ammonia production, the CO<sub>2</sub> capture process is an important part of the system. However, CO<sub>2</sub> should be stored or used in order to mitigate GHG emissions. Three scenarios to mitigate GHG are evaluated in this work for rice and wheat, *i.e.* (1) grain cultivation and production, (2) grain cultivation and pro-

Table 1 GHG emissions of paddy rice cultivation

Cultivation type	Country	System boundary	Unit	Sore	Source
Conventional	China Japan USA Thailand Bangladesh India Iran Malaysia	Up to-farm gate Cradle-to-farm gate Cradle-to-farm gate Cradle-to-farm gate Cradle-to-farm gate Production-to-farm gate No specified Cradle-to-gate	kgCO <sub>2 eq</sub> per tonne kgCO <sub>2 eq</sub> per kg kgCO <sub>2 eq</sub> per tonne tonne CO <sub>2 eq</sub> per tonne	1700-1500 1.46 1.77 2.97 3.15 5.65 <sup>a</sup> 277.21 1.39	18 and 24 29 29 30 28 31 32 33

<sup>&</sup>lt;sup>a</sup> The higher global warming is related to the lower yield, which is 50% lower than in China.

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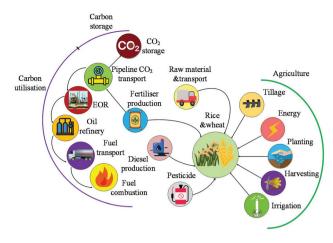


Fig. 2 Boundaries for food cultivation.

duction with CO<sub>2</sub> storage, and (3) grain cultivation and production with CO<sub>2</sub>-EOR. The system boundaries for rice and wheat are cradle-to-farm gate which include fertiliser production, cultivation, harvesting, planting, irrigation *etc*. The boundary for CO<sub>2</sub> storage starts from CO<sub>2</sub> transport to the storage site, and for CO<sub>2</sub>-EOR starts from CO<sub>2</sub> transport to fuel combustion. The functional unit for comparative analysis is 1 tonne of grain (rice or wheat). The boundaries for the system are shown in Fig. 2.

Fertilisers *e.g.* ammonium nitrate, calcium ammonium nitrate, ammonium sulphate, and urea are produced using ammonia. CO<sub>2</sub> in the process of fertiliser production is generated mainly from fossil fuels used during ammonia production, and a less percentage of CO<sub>2</sub> is generated during the production of phosphorites and sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) ammonia production.<sup>43</sup> In order to estimate the overall capture rate by incorporating CCUS in fertiliser production using SMR, a detailed assessment of the integrated process is carried out in terms of H<sub>2</sub> production and ammonia plant *via* the Haber–Bosch process. The production process is simulated in Aspen Plus to determine mass and energy balance which is based on an ammonia plant with a capacity of 1270 tonnes per day.

#### 3.1 Ammonia process

Ammonia production adopts a well-established SMR process, which is generally composed of a SMR reactor, water shift reactor (WSR),  $\rm CO_2$  separator, methanator, compressor, and ammonia reactor. Reactions (1) and (2) occur in SMR and WSR

reactors, respectively.<sup>44</sup> Table 4 presents operating parameters and assumptions used in the simulation of SMR, WSR, and carbon capture (CC).<sup>45</sup>

$$CH_4 + H_2O = CO + 3H_2$$
 (1)

$$CO + H_2O = CO_2 + H_2$$
 (2)

A schematic diagram of the whole SMR process is shown in Fig. 3 which is simulated in Aspen Plus using Peng Robinson's equation.44 The detailed processes are illustrated as follows: first methane (CH<sub>4</sub>) is mixed with steam at 510 °C and 30 bar. The mixed components enter the primary SMR reactor where reaction (1) occurs. After that, compressed air is mixed with the exhaustive flue gas from the primary SMR and flows into the second SMR reactor. O2 that comes from the air reacts with the remaining CH<sub>4</sub> to increase the temperature to 950 °C, and N2 is used to produce ammonia. The syngas basically composed of CO, CO2, H2, CH4, and H2O is cooled down to 350 °C and exchanges heat with feed water used in the SMR. Reaction (2) occurs in WSR, and the syngas is cooled at 38 °C. After that, the syngas is cleaned from CO2. The CO2 is separated from the flue gas in an absorber column by using monoethanolamine (MEA) at an efficiency of 80% to achieve the purity of 95%. The syngas that contains H2 is delivered at 17 bar to the methanator. 48 CO2 and CO are poisons for many types of catalysts. Thus, the residual CO and CO2 remaining after cleaning the syngas must be removed by converting to methane and water, as presented in reactions (3) and (4), through a nickel or ruthenium catalyst with H2 in the methanator.

$$CO + 3H_2 = CH_4 + H_2O$$
 (3)

$$CO_2 + 4H_2 = CH_4 + 2H_2O (4)$$

First, the SMR reported in ref. 49 is reproduced to validate the model developed in Aspen Plus and to estimate the efficiencies of the SMR and WSR. After that, the model is updated to the capacity of 1270 tonnes per day of ammonia based on the industrial and commercial size reported in ref. 50. Additional assumptions considered in the SMR are elaborated as follows: composition of natural gas is 100% methane; the separation of water in the condenser is complete; heat losses through the equipment are neglected. The final step is the ammonia production which consists of the following steps: syngas compression and ammonia process. The syngas contains high concentrations of  $H_2$  and  $N_2$ , which are com-

Table 4 Operating conditions of the SMR process

Parameters	Steam	NG	SMR	WSR	CC	Assumptions	Values
Efficiency (%)	_	_	_	_	80 <sup>46</sup>	Steam/CH <sub>4</sub>	3 <sup>46,47</sup>
Conversion (%)	_	_	83	73		Overall efficiency (%)	70
Pressure <sup>48</sup> (bar)	30	28.5	19.5	18	17	CO <sub>2</sub> purity (%)	95.00
Temperature <sup>48</sup> (°C)	510	510	950	$419^{44,48}$	38	-1 • • • •	

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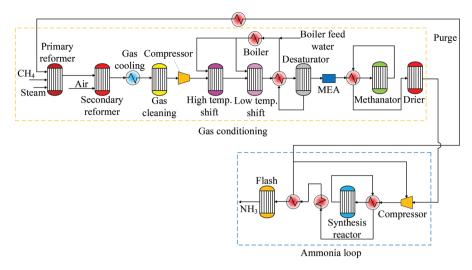


Fig. 3 Schematic diagram for ammonia production simulation.

pressed at 202.6 bar<sup>51</sup> and delivered to the finally reactor where reaction (5) takes place.

$$N_2 + 3H_2 = 2NH_3 \tag{5}$$

In this study, CO<sub>2</sub> is removed using a MEA-based capture plant. It consists of an absorber where the CO2 is captured by the amine solvent at 30 wt% and a stripper where the CO<sub>2</sub> is separated from the MEA solution.

Mass balance of the main raw material and ammonia production is shown in Table 5. It presents the main results of the ammonia process, and 28.5 tonnes per h of methane is used to generate 53.2 tonnes per h of ammonia. During the ammonia production process, 81.6 tonnes per h of CO2 is generated, and 53.2 tonnes per h is captured for utilisation and only 15 tonnes per h is emitted to the atmosphere. Although 90% of CO<sub>2</sub> is captured in the capture plant, additional fuel is burned to generate heat and steam required by the ammonia plant. Then, the overall capture rate in the ammonia plant is 77.5%. This information is used to estimate the amount of CO<sub>2</sub> mitigated in grain production, which is used for CO<sub>2</sub> storage or EOR.

Additional information for the capture plant is presented in Tables 6 and 7. The overall efficiency of the process from SMR

Table 5 Mass balance of the main raw material and ammonia production

Component	Amount
CH <sub>4</sub> (tonne per h)	28.5
CH <sub>4</sub> additional fuel in furnace (tonne per h)	3.0
Steam (tonne per h)	96.2
H <sub>2</sub> to ammonia reactor (tonne per h)	10.6
N <sub>2</sub> (tonne per h)	47.8
Ammonia (tonne per h)	53.2
CO <sub>2</sub> captured (tonne per h)	66.6
CO <sub>2</sub> emitted (tonne per h)	15.0
CO <sub>2</sub> capture (%)	77.5

to the ammonia reactor could reach 66%. The CC process is simulated to estimate energy consumption and CO2 emissions of the ammonia process. The composition and mass flow rate of the syngas are presented in Table 6, which serve as the input parameters for the CO<sub>2</sub> capture plant. The syngas flow rate is 135.2 tonnes per h, and only one post-combustion capture train is necessary to capture 90% of CO2. The size of the train is defined in the literature when considering a

Table 6 Composition and mass flow rate of the syngas to the capture plant

Items	Values
Syngas mass flow rate (tonne per h)	135.2
CH <sub>4</sub> (mol %)	0.25061
H <sub>2</sub> O (mol %)	0.62123
CO (mol %)	2.04756
H <sub>2</sub> (mol %)	62.4948
CO <sub>2</sub> (mol %)	16.5042
N <sub>2</sub> (mol %)	18.0394

Table 7 Summary of key parameters of the CO<sub>2</sub> capture (90% capture rate)

Items	Values
Syngas temperature (°C)	150
Total steam required by the capture plant (tonne per h)	212
Reboiler temp (°C)	120
Reboiler steam pressure (bar)	4
Reboiler solvent pressure (bar)	16.5
Lean solvent mass flow rate (tonne per h)	1494
Lean loading (molCO <sub>2</sub> molMEA <sup>-1</sup> )	0.27
Rich loading (molCO <sub>2</sub> molMEA <sup>-1</sup> )	0.457
CO <sub>2</sub> captured (tonne per h)	66.6
Reboiler duty (MW)	63.94
L/G ratio (mol mol <sup>-1</sup> )	6.74
Specific reboiler duty (GJ per tonCO <sub>2</sub> )	3.65
Total PCC auxiliary power consumption (MW)	0.573

(7)

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maximum of approximately 292.5 tonnes per h of the absorber column. This is mainly due to the economic limits of the size of the absorber that are based on pressure drop constraints to ensure a stable operating condition with appropriate liquid and gas distributions. Table 7 presents key results of the capture plant. The steam required to regenerate the solvent is 212 tonnes per h at 4 bar and the specific reboiler duty is 3.65 GJ per tonne  $CO_2$ . The steam required is supplied by the same ammonia process.

### 3.2 GHG emission reduction in grains by incorporating CO<sub>2</sub> storage in fertiliser production

The first alternative to reduce the CO2 from fertiliser production in this work is to incorporate CO<sub>2</sub> storage. Assuming a high capture rate of 77.5% estimated in the previous section and using information presented in Tables 1-3 (only for countries whose percentage of CO2 in GHG by fertiliser production is reported in the literature), the amount of CO2 for storage is estimated. Because the fertiliser used in rice and wheat farming depends on several factors, it cannot be assumed to be constant for all the countries. Additional emissions for transporting the CO2 from the fertiliser plant to the storage reservoir are taken into consideration based on ref. 54 and 55. Thus, it is estimated by assuming an average distance of 500 km, and an emission factor (EF) emitted per kg CO<sub>2</sub> transported by pipeline is considered. The mass flow rate of  $CO_2$  captured and transported by pipeline  $(M_{cap/grain})$  is the CO<sub>2</sub> captured and stored from the fertiliser reported in Table 8. Then, the CO<sub>2</sub> emitted through transport is estimated as presented in eqn (6) and (7) in terms of the exemplified paddy rice that is cultivated in Bangladesh:

$$\begin{split} & EC_{trans/grain} = \alpha_{e} \times M_{cap/grain} \\ & = \left[ 9.93 \times 10^{-4} \text{ kgCO}_{2 \text{ eq}} \text{ per kgCO}_{2} \right] \\ & \times \left[ 268.54 \text{ kgCO}_{2} \text{ per tonne paddy rice} \right] \\ & = 0.267 \text{ kgCO}_{2 \text{ eq}} \text{ per tonne paddy rice} \end{split}$$

$$M_{
m cap/grain} = M_{
m GHG} \times Y_{
m GHG} \times 0.9192 \times 0.934 \times \eta_{
m cr}$$
  
= 3150 kgCO<sub>2 eq</sub> per tonne × 0.11 × 0.9192 × 0.934 × 0.775  
= 230.55 kgCO<sub>2</sub> per tonne paddy rice

where EC<sub>trans/grain</sub> is the CO<sub>2</sub> equivalent emitted by transporting CO<sub>2</sub> per tonne of rice production (kg CO<sub>2</sub> eq per tonne grain),  $\alpha_{\rm e}$  is the emission factor *i.e.*  $9.93 \times 10^{-4}$  kg CO<sub>2</sub> emitted per kg of CO<sub>2</sub> transported by pipeline (kgCO<sub>2</sub> eq per kg CO<sub>2</sub>), and  $M_{\rm cap/grain}$  is the CO<sub>2</sub> captured and stored or for EOR from the fertiliser plant (kgCO<sub>2</sub> per tonne grain),  $M_{\rm GHG}$  is the total GHG quantity by grain production reported in Tables 1 and 2,  $Y_{\rm GHG}$  is the percentage of GHG by fertiliser production reported in Table 3, and values of 0.9192 and 0.934 are the percentages described in section 2.4.

It is worth noting that LCA reported in the literature for rice and wheat production includes fertiliser production. Then, the fertiliser process includes the ammonia plant. As a result, the CO<sub>2</sub> capture plant is also included since CO<sub>2</sub> separation is part of the ammonia process. In the ammonia plant, the CO<sub>2</sub> is generated at high purity as part of the process, therefore only the CO<sub>2</sub> generated by transporting is considered.

Table 9 shows the total GHG emissions with CCS.  $EC_{emit/grain}$  is the amount of  $CO_2$  that is not captured, and which is emitted to the atmosphere. When  $CO_2$  is captured and stored in the ammonia plant to produce fertilisers and use in paddy rice cultivated in Bangladesh, Thailand, and China, the GHG emission is reduced by 7.31% and in Japan by 4.62%. In the case of wheat flour cultivated in Sweden and Australia, the incorporation of CCS has higher impact on GHG emission reduction by 15.92% and 17.28%, respectively. Although the annual wheat production and the percentage of GHG reduction in wheat flour production is higher than those for rice, the total amount of  $CO_2$  generated for rice is higher than that for wheat. This is mainly because the amount of GHG generated during rice cultivation and production is much higher than that for wheat. The  $CO_2$  could be reduced

Table 8 CO<sub>2</sub> emitted by fertiliser production with CO<sub>2</sub> storage including CO<sub>2</sub> transport from the fertiliser plant to the storage site (77.5% capture rate)

Country	GHG emission by grain without CCUS	Percentage of GHG by fertiliser	Total CO <sub>2</sub> emitted by fertiliser production without capture	$M_{ m cap/grain}$	EC <sub>emit/grain</sub>	EC <sub>trans/grain</sub>	Total CO <sub>2</sub> emitted by fertiliser pro- duction with CCS
Unit	kgCO <sub>2 eq</sub> per tonne grain	%	kgCO <sub>2 eq</sub> per tonne grain	kgCO <sub>2</sub> per tonne grain	kgCO <sub>2 eq</sub> per tonne grain	kgCO <sub>2 eq</sub> per tonne grain	kgCO <sub>2 eq</sub> per tonne grain
Paddy rice							
Bangladesh	3150	$11^{a \ 28}$	297.48	230.55	66.93	0.229	67.16
Thailand	2970	$11^{b\ 30}$	280.48	217.37	63.11	0.216	63.32
China	$1600^{c}$	$11^d$	151.10	117.10	34.00	0.116	34.11
Japan	1460	7 <sup>29</sup>	137.88	68.00	31.02	0.068	31.09
Wheat							
Sweden	400	$24^{3}$	37.78	63.87	8.50	0.063	8.56
Australia	304	$26^{37}$	28.71	52.59	6.46	0.052	6.51

 $<sup>^</sup>a$  11% of CO<sub>2</sub> emission by fertiliser production includes: manufacture/transport.  $^b$  11% of CO<sub>2</sub> emission by fertiliser production includes: input of fertilisers and pesticides, rice seed production and transportation stages.  $^c$  This value is an average of 1700 and 1500 kgCO<sub>2</sub> per tonne.  $^d$  Due to the lack of information, this value is taken from information provided for Bangladesh and Thailand.  $^{28,30}$ 

Table 9 GHG emissions by rice and wheat when CCS is incorporated in fertiliser production

Country	GHG emission by grain without CCUS	GHG emission by grain with CO <sub>2</sub> storage	Reduction
Unit	kgCO <sub>2 eq</sub> per tonne grain	kgCO <sub>2 eq</sub> per tonne grain	%
Paddy rice			
Bangladesh	3150	2919.68	7.31
Thailand	2970	2752.84	7.31
China	1600	1483.01	7.31
Japan	1460	1392.07	4.65
Wheat flour			
Sweden	400	336.19	15.95
Australia	304	251.46	17.28

from 110 838 million tonnes per year to 25 018 million tonnes per year in rice, and from 24 472 million tonnes per year to 5547 million tonnes per year in wheat flour.

### 3.3 GHG emission reduction in grains by incorporating CO<sub>2</sub>-EOR in fertiliser production

As a common application for CU, EOR is selected in this work, and its general schematic diagram is shown in Fig. 4. It is one of the potential alternatives for CU and is a proven technique used to increase the crude oil production extracted from an oilfield. The EOR has been identified to be profitable at a commercial scale, which could be quite beneficial for the economy in the UK,<sup>56</sup> the United States,<sup>57</sup> Mexico,<sup>58</sup> etc. When the pressure of an oil reservoir is depleted through primary and secondary production, the use of the CO<sub>2</sub> can be a tertiary recovery method. This technology includes injecting CO2 into the reservoir to dissolve in the oil. CO<sub>2</sub> makes the oil reduce its viscosity<sup>59</sup> because CO<sub>2</sub> is miscible with oil.<sup>60</sup> Simplified calculations can give an idea related to the reduction of CO2 emissions and the benefit for the co-production of grain and crude oil. The CO2 accounted for is the one generated by transporting CO2, burning the oil extracted by injecting CO2, and the remaining 22.5% of the CO2 that is not captured in the ammonia plant.

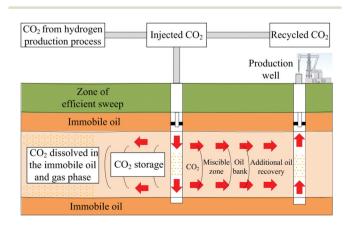


Fig. 4 General schematic diagram of EOR.

For LCA of EOR, oil and electricity are the primary product and the coproduct. <sup>54</sup> In this work, there are two products: (1) grain (rice or wheat) as the primary product and (2) oil as a coproduct. According to ref. 54 and 55, the credit (CO<sub>2</sub> reduction for CCU) in LCA related to the GHG emissions associated with the electricity is assigned only to the oil as a single product. In this work, the credit or additional CO<sub>2</sub> emission generated by oil production *via* EOR is assigned to grains. The credit or additional CO<sub>2</sub> equivalent by the incremental oil is estimated by the difference between CO<sub>2</sub> equivalent generated by EOR and by a conventional way to produce oil.

3.3.1 GHG emission reduction in grains. First,  $CO_2$  emission by grain (rice and wheat) cultivation considering a 77.5% capture rate in an ammonia plant is determined. The results are shown in Table 10 which are estimated using eqn (6) and (7). To estimate the total  $CO_2$  equivalent emitted by grains, it is necessary to calculate the  $CO_2$  equivalent generated by the incremental oil which is carried out in the next section.

3.3.2 GHG emissions in oil  $CO_2$ -EOR. The system boundary for the life cycle for the coproduct (incremental oil) starts from transporting the  $CO_2$  to fuel combustion as shown in Fig. 5a. The  $CO_2$  equivalent emitted by three segments is estimated as follows:

1. The CO<sub>2</sub> equivalent per tonne of grain by transporting CO<sub>2</sub> from the fertiliser plant to the oil field is estimated using eqn (6).

2. The  $CO_2$  equivalent emitted by the segment EOR operation is based on ref. 54 and 55 using eqn (8) and (9), and the following parameters: the incremental oil per tonne of  $CO_2$  injected  $(\phi_{uf})$  of 1.49 bbl per tonne  $CO_2$ , and the  $CO_2$ 

**Table 10**  $CO_2$  emitted by rice and wheat production with  $CO_2$ -EOR (90% capture rate)

Country	GHG emission by grain without CCUS	Percentage of GHG only by fertiliser	$M_{ m cap/grain}$	Total CO <sub>2</sub> emitted by rise and wheat production
Unit	kgCO <sub>2 eq</sub> per tonne grain	%	kgCO <sub>2</sub> per tonne grain	kgCO <sub>2</sub> per tonne grain
Paddy rice				
Bangladesh	3150	$11^{a \ 28}$	230.55	66.93
Thailand	2970	$11^{b \ 30}$	217.37	63.11
China	$1600^{c}$	$11^d$	117.10	34.00
Japan	1460	7 <sup>29</sup>	68.00	31.02
Iran	277.21	11	20.29	5.89
Malaysia	1390	11	101.73	29.54
Wheat				
Sweden	400	$24^{3}$	63.87	8.50
Australia	304	$26^{37}$	52.59	6.46
Iran	380	26	65.74	8.07
Poland	364	26	62.97	7.73

<sup>a</sup> 11% of CO<sub>2</sub> emission by fertiliser production includes: manufacture/transport. <sup>b</sup> 11% of CO<sub>2</sub> emission by fertiliser production includes: input of fertilisers and pesticides, rice seed production and transportation stages. <sup>c</sup> This value is an average of 1700 and 1500 kgCO<sub>2</sub> per tonne. <sup>d</sup> Due to the lack of information, this value is taken from information provided for Bangladesh and Thailand. <sup>28,30</sup>

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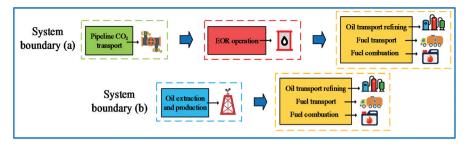


Fig. 5 System boundary of the life cycle of CO<sub>2</sub> emission (a) of incremental oil via EOR; (b) of conventional oil production.

emitted per incremental oil is 100 kgCO2 eq per bbl. For example, for paddy rice produced in Bangladesh, CO2 emitted by one barrel of incremental oil is explained by using the amount of CO<sub>2</sub> for an EOR of 230.55 kgCO<sub>2</sub> per tonne (0.230 tonnes CO2 per tonne) paddy rice which is presented in Table 11.

 $EC_{EOR/grain} = IO \times EC_{EOR/oil}$ 

- =  $[0.3435 \text{ bbl per tonne paddy rice}] \times [100 \text{ kgCO}_{2 \text{ eq}} \text{ per bbl}]$
- $= 34.35 \,\mathrm{kgCO}_{2\,\mathrm{eq}}$  per tonne paddy rice

(8)

where

$$IO = \phi_{u} \times M_{\text{cap/grain}}$$

$$= [1.49 \text{ bbl per tonne CO}_{2}]$$

$$\times [0.2306 \text{ tonne CO}_{2} \text{ per tonne paddy rice}]$$

$$= 0.3435 \text{ bbl per tonne paddy rice}$$
(9)

where EC<sub>EOR/grain</sub> is the CO<sub>2</sub> equivalent emitted by the EOR operation segment (kgCO<sub>2</sub> eq per tonne grain), EC is the CO<sub>2</sub> equivalent emitted per incremental oil produced which is defined as the amount of CO2 emitted by one barrel of oil (kgCO2 eq per bbl), IO is the total incremental oil produced by

Table 11 CO2 equivalent by oil production from CO2-EOR per one tonne of grains

Country	$E_{ m trans/grain}$	$E_{ m EOR/grain}$	$\mathrm{EC}_{\mathrm{ds/grain}}$	Total CO <sub>2</sub> emitted by oil production EOR
Unit	kgCO <sub>2 eq</sub> per tonne grain	kgCO <sub>2 eq</sub> per tonne grain	kgCO <sub>2 eq</sub> per tonne grain	kgCO <sub>2 eq</sub> per tonne grain
Paddy rice				
Bangladesh	0.229	34.35	166.61	201.19
Thailand	0.216	32.39	157.09	189.69
China	0.116	17.45	84.63	102.19
Japan	0.068	10.13	49.14	59.34
Iran	0.020	3.02	14.66	17.71
Malaysia	0.101	15.16	73.52	88.78
Wheat flour				
Sweden	0.063	9.52	46.16	55.74
Australia	0.052	7.84	38.00	45.89
Iran	0.065	9.79	47.51	57.37
Poland	0.063	9.38	45.51	54.95

using CO<sub>2</sub> captured in the ammonia plant (bbl per tonne grain),  $\phi_{\rm u}$  is a factor (bbl per tonne CO<sub>2</sub>) that is defined as the amount of incremental oil per tonne of CO<sub>2</sub> injected.

3. The CO<sub>2</sub> emitted by the last segment (oil transport refining, fuel transport, and fuel combustion) termed the downstream segment is estimated and the parameter ECoil = 485 kgCO<sub>2 eq</sub> per bbl.<sup>54</sup> For example, with respect to paddy rice produced in Bangladesh, CO2 emitted by downstream segments is explained according to following eqn (10):

$$\begin{split} & EC_{ds/grain} = IO \times EC_{oil} \\ &= [0.3435 \text{ bbl per tonne paddy rice}] \\ &\times [485 \text{ kgCO}_{2 \text{ eq}} \text{ per bbl}] \\ &= 166.6 \text{ kgCO}_{2 \text{ eq}} \text{ per tonne paddy rice} \end{split} \tag{10}$$

where EC<sub>ds/grain</sub> is the total CO<sub>2</sub> equivalent emitted by downstream segments per tonne of grain (kgCO<sub>2 eq</sub> per tonne paddy rice); ECoil is the CO2 equivalent emitted by one barrel of oil (kgCO<sub>2 eq</sub> per bbl).

Based on the same amount of oil generated by EOR, CO2 equivalent by using conventional oil production is estimated to determine the increment or the reduction of CO2 equivalent. The boundary of the life cycle for conventional oil production is shown in Fig. 5b, which covers two segments: (1) oil extraction and production, and (2) oil transport, refining, fuel transport and combustion. The CO<sub>2</sub> equivalent for the first segment is estimated based on ref. 62 and the second on ref. 54 by using eqn (9) in EOR. The GHG emission in the first is 9.2 gCO<sub>2 eq</sub> MJ<sup>-1</sup> LHV. This amount excludes oil transport because it is considered in the second segment (downstream segment). 9.2 gCO<sub>2 eq</sub> MJ<sup>-1</sup> LHV is converted to 54.3 kgCO<sub>2 eq</sub> per bbl by using the following information on oil:63 a LHV of 43.2 MJ kg<sup>-1</sup> and density of 0.86 kg l<sup>-1</sup>. Then, it is converted from kgCO<sub>2 eq</sub> per bbl kgCO<sub>2 eq</sub> per tonne grain. An example for the paddy rice from Bangladesh is described by using eqn (11):

$$\begin{split} & EC_{cop/grain} = EC_{Ccop/oil} \times IO \\ & = [54.3 \text{ kgCO}_{2 \text{ eq}} \text{ per bbl}] \times [0.3435 \text{ bbl per tonne paddy rice}] \\ & = 18.65 \text{ kgCO}_{2 \text{ eq}} \text{ per tonne paddy rice} \end{split}$$

where EC<sub>cop/grain</sub> is CO<sub>2</sub> equivalent emitted by conventional oil production per tonne of grain (kgCO<sub>2 eq</sub> per tonne paddy rice) Paper

and EC<sub>cop/oil</sub> is CO<sub>2</sub> equivalent emitted by conventional oil production per barrel of oil (kgCO<sub>2 eq</sub> per bbl).

Total CO<sub>2</sub> emitted by incremental oil production from CO<sub>2</sub>-EOR per one tonne of rice and wheat is presented in Table 11. This result together with the total CO2 emitted by the conventional approach to produce oil are used to estimate the additional CO<sub>2</sub> emission when EOR is implemented. Total CO<sub>2</sub> equivalents by conventional oil in terms of rice and wheat are presented in Table 12, and the result is lower than that via EOR presented in Table 11. The difference between the total CO<sub>2</sub> emitted by oil production via EOR and the total CO<sub>2</sub> equivalent emitted by conventional oil production is presented in Table 13 column for "Additional CO2 emitted by CO2-EOR

The difference in GHG emissions associated with oil production is assigned to grain production which leaves the LCA as a single primary product (grain). Therefore, total GHG emission by grains with CO2-EOR and the reduction of GHG emission are evaluated which are presented in Table 13. When CO<sub>2</sub> is captured and used for EOR in the ammonia plant to produce fertilisers and use in paddy rice cultivated in Bangladesh, Thailand, and China, the GHG emission is reduced by 6.81% and by 4.34% in Japan. In the case of wheat flour cultivated in Sweden and Australia, the incorporation of CCS has a higher impact on GHG emission reduction by 14.87% and 16.11%, respectively. In this paper, if the oil production to cover the demands could be supplied by conventional oil production or EOR, the CO<sub>2</sub> emissions to be quantified by conventional oil production or EOR will be based on the same amount of oil in both cases.

### Impact on grain supply chains by incorporating CCUS in the fertiliser plant

Final GHG emissions (CO<sub>2</sub> equivalent) from rice and wheat by incorporating CO<sub>2</sub> storage and EOR are presented in Fig. 6.

Table 12 CO<sub>2</sub> emissions by conventional oil production

Country	$EC_{cop/grain} \\$	$\mathrm{EC}_{\mathrm{ds/grain}}$	Total CO <sub>2</sub> equivalent emitted by conventional oil production
Unit	kgCO <sub>2 eq</sub> tonne grain	kgCO <sub>2 eq</sub> per tonne grain	kgCO <sub>2 eq</sub> per tonne grain
Paddy rice			
Bangladesh	18.67	166.61	185.27
Thailand	17.60	157.09	174.69
China	9.48	84.63	94.11
Japan	5.51	49.14	54.65
Iran	1.64	14.66	16.30
Malaysia	8.24	73.52	81.76
Wheat flour			
Sweden	5.17	46.16	51.33
Australia	4.26	38.00	42.26
Iran	5.32	47.51	52.83
Poland	5.10	45.51	50.60

When comparing both candidates, CO<sub>2</sub> storage presents a higher GHG emission reduction i.e. 6.8% than that of EOR. This is mainly because of CO<sub>2</sub> transport from the ammonia plant to old wells, and the percentage of CO<sub>2</sub> that is extracted together with the incremental oil.

It is worth noting that unlike in power generation processes where the power or thermal energy can be replaced by renewable energy such as solar and wind, it is not possible to achieve that in the ammonia plant because most of the CO<sub>2</sub> is generated from the process as explained in section 3.1. Therefore, CCUS could be the only solution to reduce GHG. For CC, it does not present any challenge in the ammonia plant since the CO2 is captured as a part of the process. For CO<sub>2</sub>-EOR, it faces a big challenge because CO<sub>2</sub> selling price is greatly dependent on the oil price. It is indicated that EOR may produce even more CO2 from the incremental oil. It is beneficial that the demand of oil could be supplied by CO<sub>2</sub>-EOR instead of increasing the oil production from EOR and a conventional alternative. Then, EOR could provide an economic incentive, and develop experience and infrastructure that would reduce the cost of this technology, especially in developing countries where grain cultivation and its price play an important role in their economy.

Another option to reduce the adverse effect of fertilisers is the use of organic fertilisers. However, for a short term, it cannot be considered as a solution since a high demand of fertilisers could only be delivered via conventional pathways. As mentioned above, this alternative option significantly leads to reduction in terms of aquatic and human toxicity, eutrophication and acidification potential among others. However, it does not bring great benefit to GWP. 18 Both alternatives of CO2 storage and CO<sub>2</sub>-EOR are important because in some countries there are no opportunities for EOR. In this circumstance, other alternatives for CU should be evaluated. The countries that supply most of the ammonia in the world are e.g. East Asia 30.6%, Africa 19.7%, East Europe and Central Asia 16% and North America 14.1%.<sup>22</sup>

Table 14 presents GHG emissions by a portion of diary food from rice and wheat using fertiliser production with CCUS.

In order to quantify the benefit of CCUS technology that could give the general insight, GHG emission reduction is presented in terms of dairy food portions made by rice and wheat flour. As shown in Fig. 7, GHG emission reduction for three spoons of rice is 24.5 grams with CCS and 22.5 grams with EOR; for 200 ml of rice milk is 17 grams with CCS and 16 grams with EOR. GHG emission reduction of 75 grams of uncooked wheat pasta with CCUS is 19 grams with CCS and 17.7 grams with CCUS. For one slice of bread, the reduction is 9.1 grams with CCS and 8.5 grams with CCUS. It is well known that CC is a technology that requires a large amount of investment. Therefore, it is very important to make people conscious about the use and optimisation of food in terms of quantifying the effect of CCUS on diary food and showing how difficult it is to reduce only around 6-7% of GHG in the rice supply chain and 14-16% in the wheat supply chain. It is concluded that CCUS could not reduce completely the GHG emissions on

Table 13 GHG emissions by rice and wheat when CO<sub>2</sub>-EOR is incorporated in fertiliser production

Country	GHG emission by grain without CCUS	$CO_2$ capture ( $CO_2$ reduced) (–)	Additional $CO_2$ emitted by $CO_2$ - EOR process <sup>a</sup> (+)	Total GHG emission by grain with CO <sub>2</sub> -EOR	Reduction
Unit	kgCO <sub>2</sub> per tonne grain	kgCO <sub>2</sub> per tonne grain	kgCO <sub>2 eq</sub> per tonne grain	kgCO <sub>2 eq</sub> per tonne grain	%
Paddy rice					
Bangladesh	3150	230.55	15.91	2935	6.81
Thailand	2970	217.37	15.00	2768	6.81
China	1600	117.10	8.08	1491	6.81
Japan	1460	68.00	4.69	1397	4.34
Iran	277.21	20.29	1.40	258	6.81
Malaysia	1390	101.73	7.02	1295	6.81
Wheat flour					
Sweden	400	63.87	4.41	341	14.87
Australia	304	52.59	3.63	255	16.11
Iran	380	65.74	4.54	319	16.11
Poland	364	62.97	4.35	305	16.11

<sup>&</sup>lt;sup>a</sup> This amount is the difference between the total CO<sub>2</sub> emitted by oil production EOR (Table 11) and the total CO<sub>2</sub> emitted CO<sub>2</sub> equivalent emitted by conventional oil production (Table 12). Because EOR emits more CO<sub>2</sub> than conventional oil, this amount is added to the total GHG emissions.

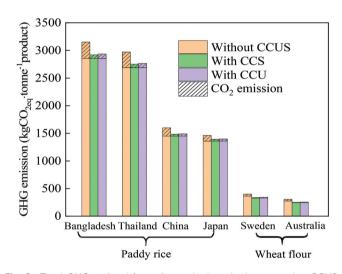


Fig. 6 Total GHG emitted from rice and wheat by incorporating CCUS in fertiliser production.

Table 14 GHG emissions by diary food from rice and wheat using fertiliser production with CCUS

Food	Portion	GHG emissions without CCUS/grams
Pasta <sup>a</sup> Bread <sup>a</sup> Rice milk <sup>a</sup> Rice <sup>a</sup>	75 gr of uncooked pasta 1 slide 200 ml 3 tablespoons of uncooked rice	118 58 236 332

food. Using correctly the amount of food in places *e.g.* homes, restaurant, and schools could be another alternative that could be complemented with CCUS.

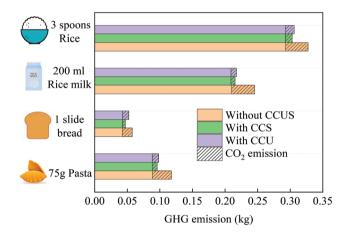


Fig. 7 GHG emissions by diary food from rice and wheat using fertiliser production with CCUS.

### 5. Conclusions

In this paper, the percentage of GHG emission reduction by incorporating CCUS in rice and wheat has been quantified. EOR has been selected as the method for CU. Conclusions are yielded as follows:

- (1) It is indicated that it is possible to reduce the GHG emissions per tonne of rice and wheat by 4.65-7.31% and 15.95-17.28% with  $CO_2$  storage as well as 4.34-6.81% and 14.87-16.11% with EOR, respectively.
- (2) Although the alternative with CO<sub>2</sub> storage presents a marginally higher GHG reduction, EOR could offer an economic incentive from additional oil production that could reduce the cost of rice and wheat when CCUS is incorporated and not necessary as an alternative to reduce GHG emissions.
- (3) With CCUS, it essentially decarbonises the fertiliser production but still has a large GHG issue.

CCS

CU

(4) Incorporation of CCUS is not only the alternative that could begin to solve the problem of GHG in food, but also could be complemented by using and optimising the amount of food in homes, hospitals, restaurants, etc.

### **Abbreviations**

CCCarbon capture

Carbon capture and storage

CO<sub>2</sub> capture, utilisation and storage

CHP Combined heat and power CO2 utilisation

EC CO2 equivalent

EF Emission factor

EOR Enhanced oil recovery

Eq Equivalent **GHG** Greenhouse gas

Global warming potential **GWP** HRSG Heat recovery steam generator

IO Incremental oil

**IPCC** Intergovernmental Panel on Climate Change

**IFA** International Fertiliser Industry Association

LCA Life cycle assessment LHV Low heating value Mass (kg·kg<sup>-1</sup>) M **MEA** Monoethanolamine

NG Natural gas

NRTL Non-random two-liquid model **SMR** Steam methane reforming

TTemperature (°C) WSR Water shift reactor

Y Percentage Emission factor  $\alpha$ Utilisation factor

cap Capture

cop Conventional oil production

cr Capture rate ds Downstream Emission e fer Fertiliser t Transport Utilisation

### Conflicts of interest

There are no conflicts to declare.

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