

# ENERGY AND CARBON BALANCE OF AMMONIA PRODUCTION FROM BIOMASS GASIFICATION

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**ABSTRACT:** This study uses life cycle assessment (LCA) tools to provide energy and carbon balances for the production of ammonia from biomass gasification compared to conventional production with natural gas. Ammonia is used for the production of nitrogen based fertilisers and whilst the fertiliser improves crop yield, the production process is energy intensive and produces 0.93 % of global greenhouse gas (GHG) emissions. The biomass system analysed includes energy crop cultivation under typical UK agronomic practice, gasification in a fast internally circulating fluidised bed gasifier to produce syngas, partial oxidation to convert the syngas into a  $H_2$  rich feedstock and combination with the correct proportion of  $N_2$  from air added in the partial oxidiser, to produce ammonia using the Haber-Bosch process. The LCA results indicate that sequestration of  $CO_2$  from the atmosphere during biomass cultivation can result in GHG savings of up to 66 % compared to conventional ammonia production. Results are also presented for the net energy balance of the system, which is a significant consideration in determining the most appropriate use of biomass amongst the sometimes competing pathways of heat, electricity or transport fuel production. Finally the scope of ongoing related work involving other ammonia production process routes and wider environmental impacts assessment is outlined.

## INTRODUCTION

Ammonia is a fundamental compound in the chemical engineering industry required for the production of nitrogen based fertilisers and approximately 147 million tons is produced globally each year ([1] from [2]). The conventional method of producing ammonia is the Haber-Bosch process, which combines  $H_2$  from steam reforming of natural gas and  $N_2$  from air. Steam reforming is very energy intensive, accounting for 1.2% of the global primary energy demand [3]. It is therefore very carbon intensive and approximately 1.5 kg  $CO_2$ /kg  $NH_3$  is released to the atmosphere [4] from ammonia production, representing 0.93 % of global greenhouse gas (GHG) emissions [2].

The depletion of fossil based fuels and the urgent need to reduce greenhouse gas (GHG) emissions to address the threat of climate change [5] have resulted in the UK government imposing legally-binding targets for carbon reductions of 80 % reduction by 2050 [6] and the European Commission setting targets of 20 % share of European energy from renewable sources by 2020 [7], with a mandatory target for the UK of 15%. While previous EU and UK climate and energy policy may have focused more on electricity, the UK government's renewable energy strategy [8] now considers a broader fuel mix, strengthening the rationale for introducing renewable fuel sources to industrial production of ammonia. One option for doing this is to use syngas from biomass gasification instead of natural gas and the work presented in this paper examines the potential greenhouse gas reductions and fossil fuel substitution that may be achieved with this method. Separately published work has assessed the environmental impacts of this [9].

Limited quantities of agricultural waste are available in the UK, and there has been a substantial focus on the cultivation of energy crops in order to increase the indigenous supply

level [10]. SRC willow is selected as the reference biomass feedstock in this study, as it is one of the main crops identified as having significant potential in the UK.

The goal of the study was to determine the net energy use and net carbon saved for the production of ammonia from biomass gasification compared to using natural gas steam reforming. The biomass gasification route included SRC willow feedstock cultivation on previously arable land, based on typical UK practice; the gasification and gas cleanup of the SRC willow to produce the product gas, including resource use and ash disposal; and ammonia synthesis by partial oxidation of the product gas. Conventional ammonia production using natural gas was based on best available European practices [11]. The functional unit in the study was 1 kg NH<sub>3</sub> produced at the ammonia plant.

## METHODOLOGY

This study uses carbon accounting methods and LCA to assess the carbon savings and net energy use of both systems. The principles and framework of LCA are described in ISO 14040:2006 [12] and this study used commercially available software: SimaPro 7.1 [13]. Databases developed by Swiss federal bodies (Ecoinvent v2.2 [14]) was used as a reference for the life cycle inventory (LCI) data and for the impact assessment methodology. The CML2 baseline 2000 impact assessment for mid-point assessment [15] was used to determine the global warming potential (GWP) for 100 years in kg.CO<sub>2eq</sub> for both systems.

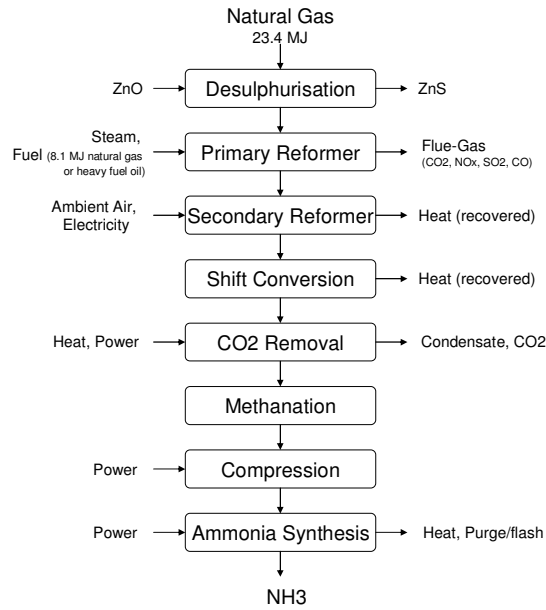
## SYSTEM DEFINITION AND INVENTORY

### Ammonia production from natural gas feedstock

Ammonia production with steam reforming of natural gas accounts for 67 % of the global ammonia feedstock [1]. Steam reforming is standard practice in industry, and the process is described in detail by the European Fertilizer Manufacturers Association [11] and summarised in Figure 1. LCI for conventional ammonia production was taken from Ecoinvent v2.2 [4, 11]. The main inputs were natural gas feedstock and additional natural gas for the primary reformer, at 23.4 MJ(LHV)/kg NH<sub>3</sub> and 8.1 MJ(LHV)/kg NH<sub>3</sub> respectively; and the total direct CO<sub>2</sub> emissions were 1.46 kg/kg NH<sub>3</sub>.

Natural gas requires cleaning and preparation prior to ammonia synthesis to remove impurities and maximise hydrogen conversion. It would be piped from the North Sea to the production plant. Sulphur is removed to prevent catalyst poisoning downstream by reaction with zinc oxide which is subsequently regenerated with a sulphur by-product. Reforming converts CH<sub>4</sub> and light hydrocarbons into H<sub>2</sub>, CO and CO<sub>2</sub> using steam supplied by additional burning of natural gas. The largest contributor of GHG emissions, in particular fossil based CO<sub>2</sub>, is from the reformer flue-gas. Other emissions include NO<sub>x</sub>, CO, SO<sub>2</sub> and CH<sub>4</sub>. In the secondary reformer further energy is supplied by internal combustion of natural gas with air to increase conversion. The nitrogen supply in the process air should equal the ammonia nitrogen content plus purge losses. The shift reactor converts CO into CO<sub>2</sub> and H<sub>2</sub> via the water-gas shift reaction and CO<sub>2</sub> is removed in either a chemical or physical absorption process to leave H<sub>2</sub>, N<sub>2</sub> and excess process steam in the process gas. Finally, methanation converts trace CO and CO<sub>2</sub>, as they are poisonous for the ammonia synthesis catalyst. Ammonia synthesis takes place by the Haber-Bosch process over an iron catalyst at pressures ranging between 100-250 bar and at 350-550°C. The process is inefficient and only 20-30 % is reacted per pass. Newly formed ammonia is separated through cooling and condensing and fresh syngas is substituted in its place, sustaining the conversion loop. Due to the exothermic reactions taking place during reforming, shift conversion and synthesis, the excess process heat is utilised for high pressure steam production, in turbines to

drive the compressors and pumps in the system. The ammonia plant could be self-sustained however small steam export and electrical import is common practice.



**Figure 1:** Schematic of ammonia production using steam reforming [11]

## Ammonia production from biomass gasification

### *Biomass cultivation, processing and delivery*

The SRC willow cultivation scheme and inventory was based on Thornley *et al.* 2009 [16] and Ecoinvent v2.2 [17] and is displayed in Figure 2. The SRC willow feedstock is cultivated on previously cultivated land and the full system specification is described in a previous study by Gilbert *et al.* [18], based on developing experience of academic and industrial partners in the Supergen Bioenergy consortium involved with crop trials and commercial supply and therefore considered reasonably representative, although there will be variation between fields, growers and regions, which will influence the LCA.

In the UK, SRC willow is typically allowed to grow for three years after cut back before the first harvest, although cycles of 2-5 years are sometimes practised. The most common three year cycle with appropriate yields has been chosen for this study. It has been assumed the crop will be maintained for seven full rotations (21 years productivity plus one year establishment and one year restoration). Typical yields are 30 odt/ha per three year rotation, at 50% moisture content, equating to an average annual yield of 10 odt/ha, as received [19]. For this study, harvesting is done with a self-propelled forage harvester with a specialist SRC header to produce 35mm wood chips. The chips are blown from the harvester into a trailer and transported 2 km to the storage area for drying. Natural drying at the storage area over a period of 30 days reduces the moisture content from 50% to 30% [[20] from [16]]. To fertilise the soil, treated sewage sludge cake (a waste from water treatment) is applied every three years after harvest. This has been shown to

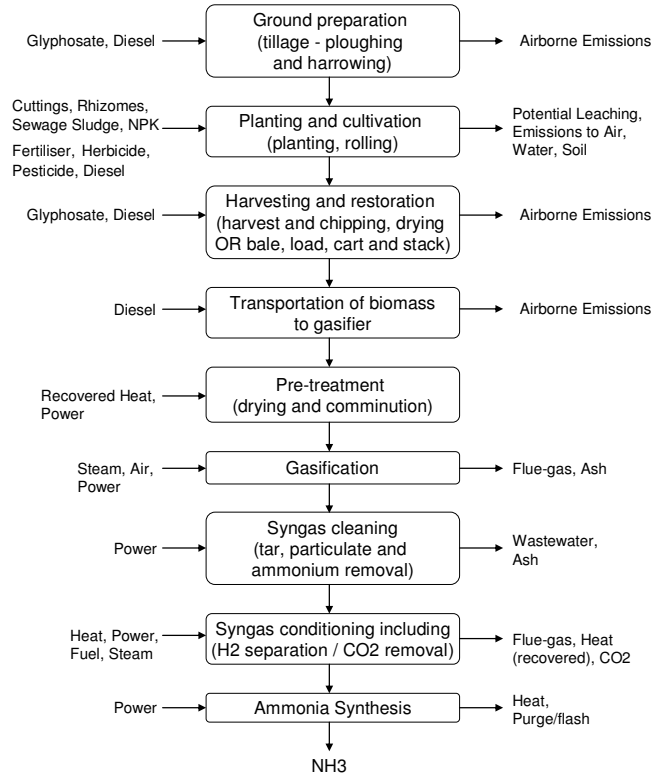
improve the greenhouse gas balance of SRC cultivation, although it increases some of the wider environmental impacts [18].

### ***Biomass gasification***

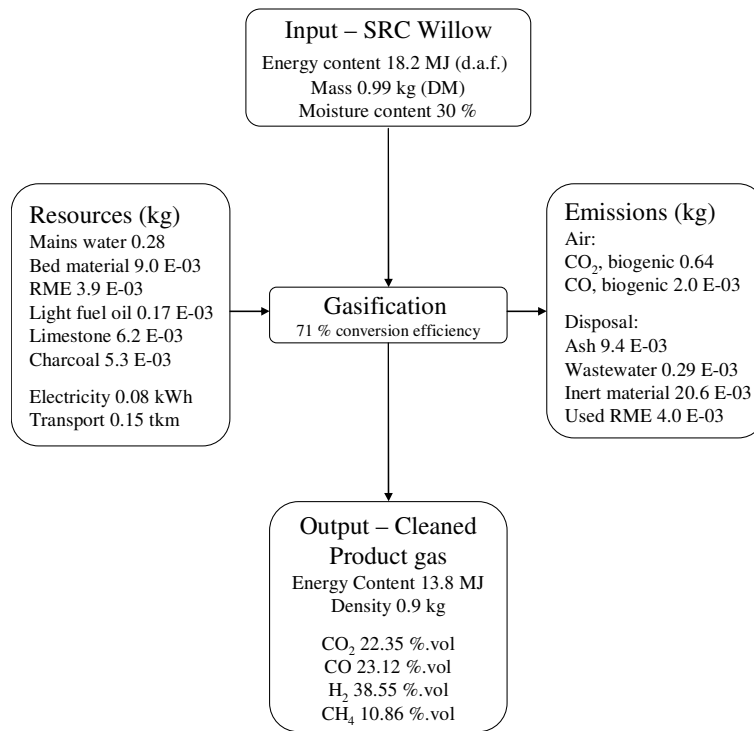
Currently available gasification technologies were reviewed to assess the viability of ammonia synthesis gas production [21, 22] and on the Fast Internal Circulating Fluidised Bed (FICFB) gasifier at Gussing, Austria, which has received successful testing with steam gasification to produce a high  $H_2$  content syngas, was selected as the reference gasifier [22-26], assuming a linear scale-up from 8  $MW_{th}$  to 40  $MW_{th}$  [27]. The main stages in this system are drying, biomass gasification with steam oxidant, char combustion in air, and syngas cleaning (including cooling, filtering and scrubbing with RME) [26]. The flue-gas from the combustion zone is used for drying and air pre-heating, and surplus heat from the ammonia production process is used to generate the steam.

With a biomass LHV of 18.2  $MJ/kg_{DM_{wood}}$  [28], moisture content of 20 % and a cold gas efficiency of 71 %, the syngas composition is: 38.55 %  $H_2$ ; 22.35 %  $CO_2$ ; 23.12 % CO and 10.86 %  $CH_4$  on a dry basis, and the calorific value is 13.8  $MJ/Nm^3$  [27].

LCI for the gasification of the SRC willow was established from mass and energy balances performed at Aston University using data from the Technical University of Vienna. Furthermore, inventory data for bed materials, electricity usage, heat for drying and steam generation, transport and infrastructure were determined using Ecoinvent v2.2 [26]. The full LCI for gasification is presented in Figure 3 for the production of 1  $Nm^3$  biomass derived syngas.



**Figure 2:** Schematic of ammonia production from biomass gasification

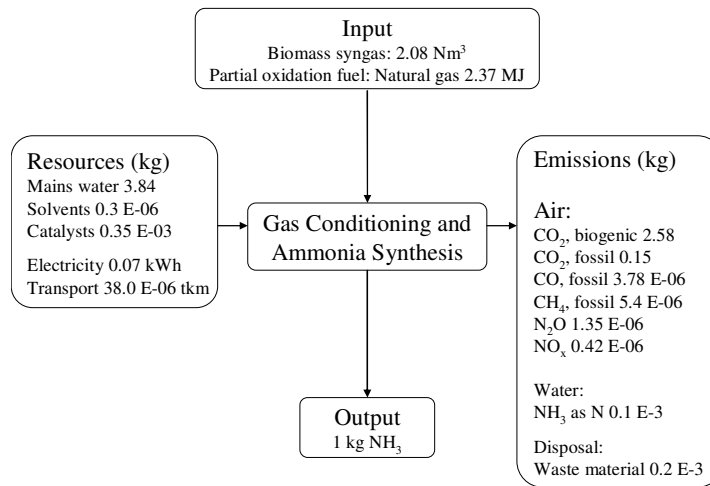


**Figure 3:** Life cycle inventory for the production of 1 Nm<sup>3</sup> syngas using Gussing gasifier

### ***Syngas conditioning and ammonia synthesis***

Following gasification, the syngas is compressed and conditioned through partial air oxidation. The H<sub>2</sub> content of the syngas is higher than natural gas meaning that two-stage reforming is not required. The same technological steps to produce ammonia from natural gas are then applied, excluding desulphurisation. The heat and steam input demands in the system were met using heat recovery. Therefore, less natural gas is required as fuel for thermal partial oxidation when compared to the fuel required for natural gas steam reforming.

The life cycle inventory was determined using mass and energy balance data from Aston University, from the European Fertilizer Manufacturers Association [11] and Ecoinvent v2.2 [4]. The full LCI for ammonia production is presented in Figure 4 for the production of 1 kg.NH<sub>3</sub>.



**Figure 4:** Life cycle inventory for gas conditioning and ammonia synthesis from biomass gasification

## RESULTS

The inventory analysis was assessed and the main fossil-based and biogenic energy use is shown in Table 1 in MJ/kg NH<sub>3</sub>. Following the inventory analysis, the impact assessment was made using SimaPro 7.1 to determine the GWP for both systems. Accordingly, the GWP for ammonia production with natural gas steam reforming was 1.64 kg CO<sub>2eq</sub>/kg NH<sub>3</sub> and the GWP for ammonia production with biomass gasification partial oxidation was 0.55 kg CO<sub>2eq</sub>/kg NH<sub>3</sub>.

**Table 1.** Net energy use for ammonia production

Energy	Unit	Natural gas, steam reforming	Biomass gasification, partial oxidation
Biomass (30 % moisture content)	kg/kg NH <sub>3</sub>		2.97
Diesel (agricultural processes)	MJ/kg NH <sub>3</sub>		0.13
Transport (biomass and sewage sludge)	MJ/kg NH <sub>3</sub>		0.38
Electricity for gasification	MJ/kg NH <sub>3</sub>		0.59 (2.3 % from renewable sources <sup>a</sup> )
Natural gas fuel	MJ/kg NH <sub>3</sub>	23.40	
Natural gas feedstock	MJ/kg NH <sub>3</sub>	8.10	2.71
Net fossil-based energy use	MJ/kg NH <sub>3</sub>	31.50	3.81

<sup>a</sup> [29]

## DISCUSSION

The net fossil-based energy saved is approximately 27.7 MJ/kg NH<sub>3</sub> using the biomass gasification system. This represents a reduction of 88%, compared to the natural gas reference case. This is mainly from switching the partial oxidiser feedstock to biomass gasification product gas. There are also additional energy savings made for the external heating required during

partial oxidation, as the  $H_2$  content of the product gas is higher than in natural gas. Furthermore, additional steam demand for partial oxidation has been maximised within the biomass gasification system, using techno-economic assessment at Aston University, to reduce the external heating requirement. The other main drivers for energy use are also summarised in Table 1 and are the diesel usage from the agricultural processes, transportation of the sewage sludge and biomass and electricity use in the gasifier for drying, grinding and compression.

Assessing the GWP, the biomass gasification system could provide a GWP saving of 1.09 kg  $CO_{2eq}/kg NH_3$  or 66%. The main drivers in both systems are related to the demands for fossil use. The foremost  $CO_{2eq}$  emissions for natural gas reforming are from the  $CO_2$  removal stage and from the burning of natural gas in the reformer. For ammonia production with biomass gasification the biogenic  $CO_2$  emissions were released during char combustion in the second stage of the FICFB gasifier and in the  $CO_2$  removal stage of ammonia synthesis. The main fossil  $CO_{2eq}$  emissions were transportation of the sewage sludge and biomass, electricity use in the system and during harvesting and chipping of the SRC willow.  $N_2O$  emissions from applying the sewage sludge fertiliser were regarded as being negligible in comparison to the carbon saved using the biomass feedstock.

It will be noted that the percentage reduction in fossil energy consumption is much greater than the percentage reduction in greenhouse gas emissions. This is primarily due to some additional greenhouse gas emissions which are incurred during SRC cultivation and transportation, including release of  $N_2O$  from soils, particularly following sludge application. It should be noted that there are substantial uncertainties associated with the actual level of emissions for this activity, dependent on soil, timing, weather etc., some of which can be addressed by good practice during cultivation.

It should also be noted that no allowance has been made in this study for any change in soil carbon levels. It is assumed that the SRC is established on previously arable land. In general establishment of SRC on arable land will lead to a long term soil carbon gain, which could legitimately be considered as part of the greenhouse gas mitigation of the overall system and would result in a modest increase in the greenhouse gas reductions achieved [30].

## CONCLUSIONS

Current ammonia production from natural gas steam reforming is very energy intensive, accounting for 1.2 % of primary energy demand. At the same time, the UK government and EU have set legally-binding targets to reduce carbon emissions of 80 % by 2050 and 20 % by 2020, respectively. There is therefore considerable scope to reduce the energy use of ammonia production by replacing the natural gas feedstock with product gas from biomass gasification. This study determined the net energy saved and GWP to produce ammonia from biomass gasification compared to natural gas steam reforming. For the system boundaries assumed in the inventory analysis, 27.7 MJ/kg  $NH_3$  of the fossil-based energy can be saved using biomass gasification equating to a  $CO_{2eq}$  saving of 1.09 kg  $CO_{2eq}/kg NH_3$ . The savings are made from the biogenic  $CO_2$  uptake during biomass cultivation and optimising the heat recovery during ammonia synthesis. The main fossil  $CO_2$  emissions are then from electricity use during gasification and diesel use during biomass cultivation and transportation to the gasifier.

There remains a need to refine this work to take into account: a range of gasifier configurations, ammonia synthesis routes and ammonia plant scales through techno-economic assessment (TEA) and LCA; an assessment of the GHG performance of the system compared to using biomass for heat, power and transport purposes and; an assessment of the wider environmental impacts; all of which are being undertaken in the Supergen Bioenergy consortium. The scale of the ammonia production plant will be evaluated, as steam reforming economies of

scale and the high-pressure Haber-Bosch process generally favour large-scale ammonia plants [31, 32]. Alternative processing configurations will also be assessed to determine the optimum potential operating conditions with regard to technology cost and carbon saved, for example, using catalytic partial oxidation instead of thermal partial oxidation to reduce the level of external heating by fossil-based combustion. Finally, as the feasibility of producing ammonia from biomass gasification goes beyond just quantifying the amount of carbon saved, future work will also assess the wider environmental impacts in comparison to the natural gas system to ensure that policy makers are aware of other key impacts involved.

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