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**Life Cycle Assessment of Sponge Nickel Produced by Gas Atomisation for Use in Industrial
Hydrogenation Catalysis Applications**

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Abstract

Purpose This paper presents a cradle-to-grave comparative Life Cycle Assessment (LCA) of new gas atomised (GA) sponge nickel catalysts and evaluates their performance against the current Cast and Crush (CC) standard currently used in the industrial hydrogenation of butyraldehyde to butanol.

Methods A comparative LCA has been made, accounting for the energy used and emissions throughout the entire life cycle of sponge nickel catalysts - ranging from the upstream production of materials (mainly aluminium and nickel), to the manufacturing, to the operation and finally to the recycling and disposal. The LCA was performed following ISO14040 principles where possible, and subsequently implemented in the software package GaBi 4.3. The CML2001 impact assessment methodology was used, with primary focus on comparing catalysts for equivalent greenhouse gasses generated over their lifetime and their relative global warming potential (GWP), and secondary focus on acidification potential (AP). This is justified as the lifetime is dominated by energy use in the operational phase, and acidification is dominated by the production of nickel for which existing ISO14040 collected data has been used. A sensitivity analysis was used to provide a number of scenarios and overall environmental performances of the various sponge nickels considered when compared to the existing industrial standard.

Results and discussion It was found that the energy and emissions during the operation phase associated with a given catalyst significantly outweigh the primary production, manufacturing and recycling. Primary production of the nickel (and to a lesser extent molybdenum when used as a dopant) also has a significant environmental impact in terms of acidification potential but this is offset by operational energy savings over the catalysts' estimated lifetime and end of life recyclability. Finally the impact of activity improvement and lifetime duration of sponge nickel catalysts was determined as both total life cycle energy for operational use and as a total life cycle Global Warming Potential.

Conclusions From this assessment, the newly-developed, higher activity spongy nickel catalysts produced by gas atomisation could have a significantly lower environmental impact than the current industry standard cast and crush method. Given the potential environmental benefits of such catalysts, applications in other processes that require a catalyst should also be investigated.

Keywords Sponge (Raney) nickel · Gas Atomisation · Cast and Crush · Butyraldehyde to butanol reaction · Celanese/Rhone Poulenc process · Life Cycle Assessment

1. Introduction

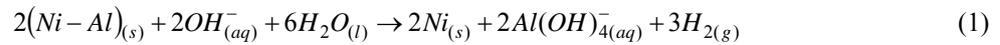
As a result of growing environmental awareness and legislative pressure more and more industries are using life cycle assessment methods. The types of processes assessed include for example: beer production (Mattila et al. 2012), concrete manufacture (Flower and Sanjayan 2007), primary aluminium smelting (Koch and Harnisch 2002) or eco-efficiency (Sailing et al. 2002). Additionally outcomes of procedure improvements like using renewable feedstocks and enzymes have been determined by LCA as highlighted in the work by Tufvesson and Börjesson (2008).

Biocatalysts (or enzymes) in particular have been the subject of a number of studies both in terms of production as is the case with the work of Neilsen et al. (2007) or application to the production of high value products like pharmaceuticals (Kim et al. 2009), waxes (Tufvesson and Börjesson 2008) or lubricants (Ekman and Börjesson, 2011). Interestingly, however, the number of industrial process assessments that include the use of non-biological or metallic catalysis has not been explored intensively. Authors have concentrated primarily on estimating the necessary inventories involved in fine and speciality chemical production like solvents (Geisler et al. 2004, Wernet et al. 2012) or the environmental impact of petrochemical solvent production as a whole (Capello et al 2009). The effect of improvements in metallic catalytic activity has not been subject to the same level of interest as that of biocatalysts. The purpose of this study is to perform a LCA of different sponge nickel catalysts, which are manufactured by two distinct processes: Cast and Crush or Gas Atomisation. The effect of both of these processes on Global Warming Potential (GWP) is investigated in relation to the production of an industrial solvent, butanol

Sponge or Raney® nickel has been used as a catalyst for hydrogenation in industrial-scale chemical reactors since the 1920s when it was first developed and patented by Raney (1925) and Raney (1927). According to the US Geological Survey, it is estimated that about 2.5% of primary nickel metal use is for nickel catalysts, the majority being sponge nickel, which amounted to about 2144 tonnes of nickel in Europe in 2001 (Larsen and Tyle 2008).

The traditional method of manufacturing sponge nickel is to cast a nickel and aluminium ingot of a particular composition, typically 50:50 wt. %, the ingot is subsequently crushed to a fine particle size of the order of 50-100 µm, resulting in the typical morphology shown in Figure 1a. The Ni-Al powder is then leached using an

aqueous sodium hydroxide solution to remove the aluminium, with the caustic leaching reaction being described by Devred et al (2009) and Devred et al (2010):

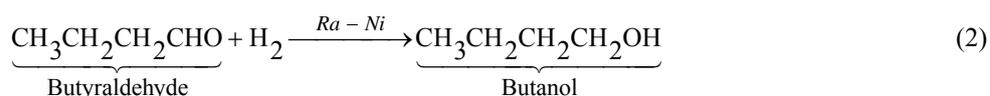


This leaching removes almost all of the aluminium from the powder, leaving a porous structure with a very high surface area, which is linked to the catalytic activity of the powder (Barnard et al 2011).

Ni-Al powder produced by Gas Atomisation (GA), shown in Figure 1b, is an alternative process which is proving to have a number of advantages over the conventional Cast and Crush (CC) route. Gas Atomisation is an established method for the production of metallic powders where a stream of molten metal emerges from a nozzle into a collection vessel. High velocity gas is directed at the molten metal stream (molten Ni-Al alloy in this case) as it emerges from the nozzle. The gas impingement acts to break up the liquid stream into a fine spray of liquid metal droplets. The droplets are very rapidly cooled by the gas and solidification rates are extremely high, of the order of 10^6 Ks^{-1} . These high solidification rates produce extremely fine metallurgical microstructures within the solidified particles, much finer than those produced via conventional ingot casting processes. The solidified particles are collected at the bottom of the vessel in the form of smooth spherical particles. For the Ni-Al alloys used in this work particle diameters typically ranged anywhere from $<5 \mu\text{m}$ up to $300 \mu\text{m}$. Whether the powder is produced via the GA or CC route it still requires caustic leaching to remove aluminium and produce a nano-porous nickel structure. As a powder production route GA has several advantages:

- It avoids the crushing of an ingot.
- It allows greater control on the distribution of particle sizes, reducing the labour intensive bin sifting for specific particle sizes.
- It allows greater control of the cooling rates of individual particles allowing manipulation of the microstructure, which in turn allows the creation of greater surface areas in the leached particles and ultimately greater catalytic activity.

Sponge nickel is used as a heterogeneous catalyst in many industrial hydrogenation reactions and in this study one of the most topical reactions, the butyraldehyde, $\text{CH}_3(\text{CH}_2)_2\text{CHO}$ to butanol, $\text{C}_4\text{H}_{10}\text{O}$ reaction (2), has been chosen for assessment by the LCA matrix. As a product, butanol is a versatile chemical feedstock and solvent which finds use in paints, printing inks, textiles, coatings, sealants, plastics and adhesives. As a result butanol is required worldwide; with current global demand in excess of 1.2 billion gallons per year and a market value of over \$6 billion annually (BioButanol 2011)



In addition other hydrogenation reactions can be performed with sponge catalysts made from metals such as cobalt and copper using the Raney process, or with noble catalysts such as platinum and palladium (Chen 2006), with the appropriate catalyst chosen on the basis of low cost and highest functionality. For the latter the main parameters are the catalyst's activity, selectivity, lifetime and surface area, for the required reaction. Catalytic activity is a function of the hydrogen which is absorbed at the micro-surfaces of the catalyst during preparation that can be of the order of 25-100ml of hydrogen per gram of nickel and it is this that promotes the hydrogenation reaction. The more hydrogen which is pre-absorbed, the greater the activity, however over time the catalytic activity will reduce due to formation of inactive materials like nickel-aluminate (Forzatti and Lietti 1999) or surface contamination (Somorjai GA and Li Y 2010) resulting in gradual catalyst poisoning in the reactor or break down of the catalyst's integral structure. Selectivity is largely determined by the metal used, but is also influenced by the reactor's operational conditions like temperature and hydrogen pressure that can vary from between 40 - 350 °C, and 0.5 to 4.5 MPa, respectively.

The aim of this paper is to carry out a comparative Life Cycle Assessment (LCA) of new gas atomised sponge nickel catalysts and evaluate their performance against the current standard currently used in the industrial hydrogenation of butyraldehyde to butanol. The goal is to establish whether the increases in activity/performance of the catalysts seen in the laboratory could give rise to any significant environmental improvements over standard catalysts; with both un-doped and doped catalysts (where elements like Fe, Mo, Sn or Ti are added to further enhance catalytic activity) considered as part of this assessment.

2. Methodology

Generally following ISO14040 guidelines, the goal of the LCA was defined as “to understand the environmental impact of the standard sponge-nickel catalyst over its lifetime as applied to the production of butanol via hydrogenation, and how modifications to the standard catalyst could lower the overall impact”. The scope in this application of sponge nickel as a catalyst was limited to a single reaction on an industrial scale, the butyraldehyde to butanol reaction, although there are many other possible reactions which sponge nickel is used for.

The compilation of **inventory data** for each of the steps in the process was done with the objective of prioritising process data which had itself been derived to ISO1040 standards. The benchmark standard catalyst chosen for comparison was one produced via the CC route, as opposed to the novel catalysts which were produced via the gas atomisation route. The LCA was carried out from the perspective of the catalyst alone, based on the butyraldehyde to butanol production route with the energy mix determined from the BUWAL/GaBi database i.e. it did not include the materials or life of the reactor itself and from a temporal perspective was based on the number of batches the catalyst would survive in a particular reactor. The BUWAL data for energy generation was chosen as it was the closest geographical match to a similar major production plant exists (USA – Texas) available at the time of the work.

There are many established impact assessment methodologies available including CML2001, EDIP97 and Eco-indicator99, for which more details can be found in Dreyer et al (2003). The first two are so-called mid-point approaches, and the latter is an end-point approach. In this work we have primarily used the CML2001 approach, which is justified as the Climate Change impact category is less susceptible to the differences between methodologies as are impact categories like Human Toxicity and Ecotoxicity.

Where the LCA departs from standard guidelines is due to the fact that key data in the lifecycle is predictive, as the catalysts being examined are still at the laboratory/pilot scale as opposed to mass production, and there has not been to date a complete LCA done by the catalyst producers for this particular catalyst. Furthermore, a high level of uncertainty for the data of some processes was unavoidable, and estimating parameters were very difficult to find in public domain sources particularly in the operational and recycling stages of the lifecycle.

Another departure from the ISO14040 guidelines is that it has not been possible in this study to implement due process involving independent verification (via third parties and life-cycle inventory committees) of data measurements made at process level of production, waste, energy and emissions. These limitations result primarily from a lack of specific data like material and energy flows within a butanol producing plant which are unknown - best estimates can only be made from a small number of sources, hence the level of energy saving calculated could be too high and verified flow figures for recycled catalysts are difficult obtain. In addition, argon is used in significant quantities throughout the process at various points and from various sources but the impact as been simplified to a power input requirement equivalent to 0.102 kWh/kg.

Nevertheless, the results of this work should still be of significant interest to what is a large industrial sector.

3. Life Cycle Assessment

The life cycle phases of a sponge nickel catalyst were implemented in GaBi 4.3 (PE International 2008) are outlined in Figure 2, together with a list of key processes and data requirements at each stage. As illustrated, energy is required at all stages in various forms and from various sources, with emissions produced at each of the stages. The approach has been to compile inventory data and process information for all primary materials and consumables – where possible - and monitor calculated Gross Energy Requirements (GER), with reference to as wide a range of sources as possible.

3.1 System Boundaries

When it came to emissions, global outputs were assumed, and inventory data was used from available ISO14040 life-cycle inventory data where possible, e.g. aluminium (Sauer 2003). It is understood that there may be a level of deviation from a European-based production route over global averages, as suggested by both the Aluminium (Sauer 2003) and Nickel Institutes' (Ecobalance 2000) in their life-cycle assessments, and that these deviations could be large on a world-wide scale. These deviations can be understood, for example, by considering the production of aluminium. For aluminium 85% of the energy requirement is from the electrolysis process, and the differences in emissions are large, depending on whether this electricity is produced from hydroelectric power or from fossil-fuel power stations. To this extent, the use of available data should be approached with care as it often does not account for countries such as China and Russia which may possess very different electrical power generation mixes to other countries and for which data is often unavailable. Furthermore, as the location

supply chain is not fully known, transport of materials has been omitted, though it is possible that this could add 10-20% more Global Warming Potential (GWP) emissions for the catalyst production.

Although there have been predictions for growth, the demand for butanol has remained relatively static over the preceding five years – 2006 to 2011 - with a growth rate of 0.6% and world production is currently only operating at 82% capacity (Liu and Xue, 2012). Thus from a temporal perspective, the material flow was assumed to be in a steady state, and in the application of the industrial hydrogenation, the LCA model was constructed to allow some recycled nickel to remain within the system boundaries in a closed-loop, but with other material (nickel and molybdenum) flowing out in an open-loop towards downgraded products (e.g. steel). The overall system boundaries for the LCA study are shown in Figure 3 (a) with further details of the primary material production and manufacturing processes for sponge nickel displayed in (b) and (c), respectively.

3.1.1 Industrial Hydrogenation of Butyraldehyde to Butanol

The butanol production route chosen for this study was the Celanese/Rhone Poulenc process, which is a two step process:

Step 1) synthetic gas or syngas (a mixture of carbon monoxide and hydrogen) and propylene react together in the presence of a rhodium catalyst to produce butyraldehyde, and,

Step 2) the butyraldehyde is then hydrogenated using a sponge nickel catalyst to produce butanol.

Both the butyraldehyde (Step 1) and butanol (Step 2) production are typically performed within the same plant, however, the primary subject of this LCA is the effect of sponge nickel activity on the efficiency of the butanol process (Step 2). Thus, the butyraldehyde production process (Step 1) has been considered to be independent from the butanol production (Step 2), and left outside the LCA system boundaries, justified as the catalysts used in both steps are completely different. Although it is understood that this represents an omission of baseline emissions and its inclusion would require a similar second LCA study, it is one which still allows the relative comparison between standard and new nickel catalysts used in the butanol production.

3.1.2 Function and Functional Unit

In the context of this LCA, the function of the sponge nickel catalyst is defined to be the production of butanol via hydrogenation. The overall functional unit of the LCA has been chosen to be 1 kg of sponge nickel.

3.2 Life-Cycle Inventory Data

3.2.1 Upstream Materials

It is not within the scope of this paper to list the full inventory of data used, which includes extraction routes and metallurgical processes for the recovery of each of the primary metals used in sponge nickel. Some of these are readily available, but a summary of overall gross energy requirements (GER) in MJ/kg of product, and an average of quoted green house gases (GHG) in kg CO₂-equivalents per kg of product, as detailed in Table 1 are given for comparison.

Aluminium

The data for a primary ingot of aluminium was obtained from the International Institute of Aluminium LCA report (Saur 2003). The mining data for Bauxite comes from 10 mines (49% of world-wide operations), the alumina refining data came from 24 refineries (59% of world-wide operations), the electrolysis information for aluminium production came from 75 electrolysis plants (55% of world-wide operations), but any production by China is not included in the data. In this work, the representative method of aluminium production was the Bayer process for alumina production, followed by electrolysis (the Hall-Heroult process) for the alumina reduction to aluminium, followed by casting of the aluminium into an ingot.

Nickel

The data for a primary nickel was obtained from the Nickel Institute LCI report (Ecobalance 2000). For nickel production, the class 1 (>99%Ni) nickel product was chosen, as opposed to ferronickel or nickel oxide. The LCA data is for 2000 and represents 56-64% of the total annual world production of nickel, but does not include specifically China or Russia. The processing routes were very different and the data represents an average of different extraction routes (pyrometallurgical and hydrometallurgical) coming from two different types of ores (sulfidic and oxidic).

Dopants (Mo, Ti, Sn, Fe)

Dopants are typically used to boost catalytic activity, usually at levels of 1-3 wt. %. The IMOA molybdenum (Mo) data only went as far as the production of technical grade molybdenum trioxide (MoO_3), so two further processing stages were required, namely a *sublimation* phase to obtain pure MoO_3 and a *reduction* stage to obtain pure Mo powder. Titanium was assumed to be produced by the Kroll process, and implemented using data by Norgate et al. (2004a; 2007). Tin (Sn) data was part of the existing GaBi Lean Database, and was compared to available life-cycle inventory data from the tin institute (ITRI). An iron inventory was put together on the basis of the production of pig iron in a blast furnace, with data from Norgate et al (2004b) are assumed to be representative. Dopants are being considered here for completeness. However, the amounts used contribute only a relatively small environmental GWP burden. There is however a penalty associated with recycling and disposal which is discussed below.

Consumable Materials

Available inventory data from the GaBi Lean Database was used for industrial water (pure, processed), sodium hydroxide (caustic soda), and hydrogen. The only consumable which is used in large quantities during gas atomisation is argon, for which no data was available. However, according to Agrawal et al (1989) and Häussinger et al (2000), cryogenic production of Argon requires 0.102 kWh/kg.

3.3 Manufacturing

3.3.1. Gas Atomised (GA) Powder Production Route

The inventory data presented in Table 2 have been derived from a variety of sources (Yule and Dunkley 1994; Pourghahramani 2006; Devred et al 2009). Out-of-range particles are collected and can be re-melted in a subsequent batch, leading to an overall yield of 95%. Thermodynamic properties (specific heat capacity and latent heat) were used to calculate the theoretical energy requirements for melting. The gas atomisers used in this study are assumed to use induction melting (typical efficiency of 50%), and this was then used to get an estimate of the practical melting energy. The values obtained matched published melting energy requirements (Dunkley and Aderhold 2007). As the melting is done under argon, levels of alloy loss by evaporation have been assumed to be negligible (<0.1%), where this lost material is collected in cyclone filters at the end of the run. The measurements were based on a small pilot scale gas atomiser, which does not have a gas recycling unit fitted. These units are expensive and while allowing 98% of the gas to be recycled, the cycle is not indefinite and the system eventually requires a complete refill, otherwise there are unacceptable losses in quality. By using such units argon use would be lowered substantially in a scaled operation to less than 0.007 kg/kg Ni-Al alloy.

3.3.2 Cast and Crush (CC) Powder Production Route

This route consists of two steps, melting (casting) and crushing (i.e. milling/grinding/attrition). Similar to the GA route, the induction melting was assumed to be done in a crucible under argon at an efficiency of 50%, and the energies were estimated from thermodynamic properties of NiAl, as 0.60-0.8 kWh/kg. The grinding/crushing steps have been estimated at 0.044 kWh/kg, (Pourghahramani 2006), based on the averaged energy requirements for mechanical alloying of all materials to various particle sizes. This may be an overestimate as Ni-Al is known to be brittle and thus requires lower than average attrition energies.

3.3.3 Caustic Leaching

The caustic leaching process is applied to both CC and GA produced Ni-Al powders. It is a batch process, processing anywhere up to a tonne at a time and the aluminium is almost completely removed from the metal by using an aqueous 20-30 wt. % sodium hydroxide (NaOH) solution to give both sponge nickel and the lower value by-product sodium aluminate (NaAlO_2). Referring to the reaction described by equation (1), sodium aluminate can be retrieved from aqueous solution to be used for the recovery of aluminium, but within the catalyst manufacturing sector it is usually sold as a by-product for paper manufacturing and water treatment processes. The reaction is strongly exothermic, however, the addition of NaOH is done in a controlled manner to maintain the temperature of the solution at about 80°C and after 3 hours the leaching process is complete. The sponge-nickel is then washed and stored in distilled water. In practice, a higher weight percentage of NaOH is used in order to reduce the appearance of aluminium hydroxide ($\text{Al}(\text{OH})_3$) precipitate, which can block pores in the sponge nickel and lead to degradation of catalytic performance.

3.3.4 Hydrogenation of Butyraldehyde to Butanol

According to McCann (2000), 1020 kg butyraldehyde is required in the production of 1000kg of butanol together with or 35.4 kg ($\equiv 394 \text{ Nm}^3$) of hydrogen. In the Celanese/Poulenc production process, butyraldehyde is produced from propylene and syngas (from coal gasification), in processes upstream within the same plant where both require substantial energy (10-18 MJ/kg Syngas, ~40-50 MJ/kg butyraldehyde). However, for the purpose of the LCA of the catalyst in the butanol process, these upstream processes have been set outside the system boundaries. The typical weight percent of the nickel catalyst is 2-10%, and a nominal loading of 10% has been used, which, for a batch size of 1 tonne is 100kg.

The outline of a typical vapour phase hydrogenation reactor is shown in Figure 4, (Cropley et al. 1984) and highlights the energy and raw material inputs. Most hydrogenation reactions are exothermic, so the reactors need to be cooled to keep the catalyst at the required temperature, usually 5-10°C above the dew point in order not to sinter or bind the catalyst particles together causing a decrease in effective surface area, which would decrease the catalytic lifetime. The heat required to initially heat the butyraldehyde and hydrogen to 135°C is obtained from a feedback loop as steam in the pre-heater. The specific heat capacity of butyraldehyde is 189.14 J/mol K therefore the energy required to raise every 1 kg (13.9 molar equivalents) from ambient temperature (25°C) to 135°C is 289.195 kJ. In contrast, the enthalpy of the reaction is -70.15 ± 1.3 kJ/mol, (Buckley and Cox 1967, Afeefy et al. 2000), meaning that for every 1 kg of butyraldehyde consumed to produce the butanol, 975.09 kJ of heat is generated. Based on the patent by Ueda and Sadaie (1999), typical net energy requirements are 8 MCal/hr (0.0178 kWh/hr) for a single column reactor with a 21.3kg/hr butyraldehyde feed, which works out at about 1.372 MJ/kg-feed (0.381 kWh/kg-feed). From Motz (2000), 0.70kWh/kg (2.52MJ/kg) is required for the compressor, and about 0.420kWh/kg (1.512MJ/kg) for the cooler, supplied by electricity. Thus, an operational net electrical energy requirement for a standard catalyst of 0.361 kWh/kg butanol was used for the LCA model, which should be compared to the value of 0.111 kWh/kg calculated from data published by Gielen et al. (2006).

During the course of the IMPRESS project (Jarvis and Voss 2005), it was found that sponge nickel produced from gas atomised powder gives superior activities to the standard CC product. The effect of an increased activity of the catalyst has been assumed to decrease the required residence time in the reactor and hence overall power consumption, primarily for the compressor. These increases in relative activity were used as a basis to approximate the levels of energy consumption reduction possible with different sponge nickel compositions (with and without the addition of a dopant) and the results of these estimations – normalised to a standard industrial catalyst - are shown in Table 3. It should be emphasised that these are estimates based on the limited literature available, and as yet still require validation.

Catalysts eventually become contaminated (e.g. with sulphur and carbon) and this leads to a degradation of performance with the catalyst eventually requiring refreshing or replacing with new catalyst. It appears that many factors affect the deterioration of the catalyst including the purity of feedstock, the levels of temperature and pressure control in the reactor and of course different hydrogenation reactions will produce different useful lifetimes of catalyst material. With regards to the lifetime of the catalyst in the reactor, estimates were based

upon the work of Agnic and Resnik (2006), regarding the durability of catalysts in a large scale reactor. According to Agnic and Resnik (2006), sponge nickel catalysts can be re-used 16 to 22 times. The lifetime of the catalysts were assumed to be 3 months, although according to some sources (Marafi and Stanislaus 2008; Hassan and Richter 2002) they can last up to two years.

3.4 Recycling

3.4.1 Regeneration of Spent Catalysts

According to Hassan and Richter (2002), in 2002, up to 9000 t/y of non-precious catalysts were being used in Germany alone, and only a small fraction of these were being recycled because the cost at that time of land-fill and special treatments to stop heavy metals leaching into soil were much cheaper than the recycling processes. In 1996, the level of spent catalyst being generated from a Hydrotreating processes was estimated at 87,500 t/y worldwide, but, according to Marafi and Stanislaus (2008) this had doubled to up to 170,000 t/y by 2007.

A combination of the high prices of metals over the last decade, the increase in spent catalyst availability, increases in the cost of landfill due to increasing regulation of the disposal of hazardous substances and improved recovery technology has led to spent catalysts acquiring a positive net value and being treated as a commodity, particularly those containing molybdenum and vanadium. Many catalyst production companies now offer integrated life-cycle management of their catalysts, with the regeneration of the catalyst being done by a specialist company “ex situ”.

Recycling spent catalysts can be done by either pyrometallurgical or hydrometallurgical routes. Regenerated catalysts are up to 70-80% as active as fresh catalyst, but are available at 50% of the cost. Regenerated catalysts are often added to the fresh catalyst in quantities as high as 50%. Nickel recovery from recycling is currently as high as 90%, and the energy consumption is only of the order of 10 MJ/kg as opposed to 200 MJ/kg for primary Ni production.

3.4.2 Disposal

Uncertainties in the overall quantities of sponge nickel catalysts being supplied by EU manufacturers that is disposed of in expensive landfill (due to the known dangers of molybdenum, nickel and chromium leaching from landfills linked to human toxicity (McLaughlin 2004) is uncertain. So due to the absence of actual yearly

figures, it has not been possible to include the heavy metal loss to water estimates for landfill resulting from catalyst disposal.

3.5 Inventory Data Analysis

It is important to make a distinction in the quality of the data implemented in the current LCA. The data is deemed to be of high quality for two of the main primary materials used to manufacture the catalyst (aluminium and nickel), both implemented from full ISO14040 LCA as conducted by the International Aluminium Institute and the Nickel Institute. The data is relatively good for consumable materials (water, sodium hydroxide, hydrogen – all part of GaBi lean database) to poor (Argon – only production energy considered: Agrawal et al (1989) and Häussinger et al (2000)). The data for doping materials ranged from good (Molybdenum from the International Molybdenum Association, Landfield Grieg 2008), to medium (data for Tin available as part of GaBi lean database) to poor (Titanium and Iron – separate LCA data built from sub-models from various sources).

The relatively much greater use of the primary metals (aluminium and nickel) over doping materials and consumables would indicate that overall upstream material data can be considered to be relatively good, certainly valid for a comparative basis between the industrial standard and improved catalysts.

The data gathered for the manufacturing steps is also deemed to be of reasonable quality, as it came directly from requested measurements of energy and materials consumed by partners in the LCA project. However, the consumables and process energy usage are biased towards electrical energy usage, and hence more suitable to a “carbon footprint” analysis, and this is a poor indicator for other environmental impacts, as previously outlined by Laurent et al (2012).

The poorest inventory data is known to reside in the recycling and disposal phase, where a very high 99% recovery has been assumed, 49% being downgraded and 50% returned to catalytic applications, 1% disposal/lost. As the emphasis of the current LCA is in comparing catalysts, it is thought that the 1% loss would not significantly change from one catalyst to the other, nor the final outcome and resulting interpretation.

4. Results and Discussion

The total energy required to make 1kg of sponge nickel is estimated from both the total energy used in primary production and manufacturing, which for CC is 669.19 MJ, and for the gas atomised route 854.18 MJ, respectively (see Figure 5), representing a 27% increase.. This is dwarfed by the energy used during the operational phase of the catalyst in the reactor, which during the estimated lifetime of 1kg of catalyst, could potential produce over 10,000kg of butanol (based on a lifetime of approximately 3 months generating ~100 kg/day), and the reactor uses 6MJ per kg of butanol, i.e. 60,000 MJ in total (Please notice that in Figure 5 the operational output has been expressed as MJ per kg of Ra-Ni × **ton** of butanol product). Thus, the catalyst production energy only represents 1% of the total energy required.

The caustic leaching process is performed in batches and depending on the starting alloy composition a higher content of aluminium is “wasted” per kg of sponge nickel produced. This additional energy required (in terms of sodium hydroxide and leaching time) means gas atomisation exhibits varying warming potentials per kg of sponge nickel catalyst produced. This can be seen in Figure 6, which shows an increase from ~ 25 to ~ 37 kg CO₂-Equivalents when the alloy changes by 20 atomic percent from Ni-68.5Al to Ni-82.5Al. These results also highlight that the presence of dopants - which increase the level of energy saving during the operational phase as shown in Table 3 - can also decrease the Global Warming Potential of sponge nickel alloys when compared to the equivalent non-doped alloy, due to reduced leaching times and associated energy demands.

To determine the environmental impact of gas atomisation sponge nickel production only across various categories the SP-GA6 (Ni-75Al-1.5%Mo) alloy was chosen as an example and the results are displayed in Figure 7 as (a) impact categories and (b) relative contributions across the categories considered. It is clear that from the production perspective the nickel contribution has the highest contribution towards acidification potential which is the result of the liquid-liquid extraction techniques currently used on sulfidic ores. The extraction of molybdenum also produces a relatively large acidification potential though this is offset somewhat as dopants are only required in low amounts and can lead to large energy savings during the operation phase (~70 kWh/ton butanol) and the potential for recyclability.

Although the upstream data does incorporate data of reasonable quality which accounts for the other environmental impact categories (particularly AP), the study would benefit from a more detailed assessment of

the results. However, again, the small increases in AP arising from increased use of nickel and molybdenum in the new catalysts are small compared to the operational use phase of life.

The overall life-cycle energy requirements for the production of 1 kg of butanol are shown in Figure 8, as a function of an increasing number of batches for which the catalyst survives. Once a catalyst has survived more than 10 batches, there is a cross-over, and the more active catalysts use lower energy consumption per batch (6 MJ/kg-butanol). Furthermore when the lifespan exceeds more than 100 batches, then the impact categories closely follow the activity trends of the catalyst and the relative contributions are dominated by the energy mix of the reactor and hydrogen production, as opposed to catalysts with a shorter lifetime in which manufacturing and material production are also visible.

As outlined previously, caustic leaching is a batch process, the greater the aluminium weight content in the initial melting alloy, the less sponge nickel is produced with each batch. Thus, there is an associated environmental overhead in using a greater weight percentage of aluminium in the ingot, from the perspective of primary production emissions, additional melting energy and additional caustic soda. Gas atomisation also has a slightly greater energy requirement as a manufacturing process. Nonetheless, as can be seen from the results in Figure 9 for the hydrogenation of butyraldehyde to butanol considered by this paper, the intended lifetime of the catalyst in its application guarantees that the energy required in its production is small to insignificant in comparison with the energy associated during its operation phase, which is directly related to the energy required in providing the hydrogen in the first place. In addition, the results in Figure 9 illustrate that the initial aluminium content of the master alloy and the presence of dopant can have a profound effect on the operational energy usage and as a consequence lead to a reduction in the amount of associated CO₂ equivalents produced, e.g. ~300 kg CO₂ equiv for SP-GA6 (Ni-75Al-1.5%Mo) *cf.* SP-GA3 (Ni-75Al). The maximum difference between the industrial standard and the new gas atomised catalysts was about 500 kg CO₂ equiv over the catalysts lifetime.

The total lifetime energy expended is inversely related to the catalysts' activity, i.e. the higher the activity the less energy is required to produce the same amount of the butanol. Although the effect of selectivity has not been investigated, the durability of the catalyst is vitally important.

Overall, and in summary, the total energy associated with primary material production and manufacturing of the new gas atomised catalysts has been found to be up to 27% higher than the industry standard and leads to GHG emissions which are up to 48% higher (an increase of 37 kg CO₂-equiv per kg of sponge nickel). However, the dominating energy requirements of the operational life phase mean that this could lead to a 10% decrease of GHG emissions over its lifetime (decrease of 500 kg Co₂-equiv per kg of sponge nickel used) compared to the industry standard.

5. Conclusions

From the results of the comparative LCA it can be concluded that although the production of 1kg of sponge nickel catalyst by a Gas Atomisation (GA) route requires initially initially 27% more energy when compared to that of the production of 1 kg of standard Cast and Crush (CC) method, sponge nickel offers a much higher catalytic activity. It is this improvement in catalytic behaviour that - based on the estimates outlined in this paper – have the potential to offer a reduction of the operational energy consumption, a 10% decrease in GHG emissions and hence an associated decrease in the Global Warming Potential (GWP) of the butyraldehyde hydrogenation process over the complete lifetime of the sponge nickel catalyst when compared to the current industry standard. These findings also indicate that sponge nickel catalysts could provide further environmental benefits to other processes which require catalytic membranes like alkaline fuel cells.

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Table 1 – Gross Energy Requirements (GER) and Global Warming Potential (GWP) of materials in this LCA.

Principal product	Production process	GER	GWP	References
		(MJ/kg per kg product)	(kg CO ₂ -eq. per kg-product)	
Primary Metals				
Aluminium (Al)	Bayer,	180	22.4	Kellogg 1974;1977;1984

	Hall Heroult			Valero et al 2002; Norgate et al 2007
Nickel (Ni)	Smelting/refining Pressure leaching	114-239	11.4	Norgate et al 2000; 2004c
Dopants				
Titanium (Ti)	Becher and Kroll	361	35.7	Norgate et al 2004a
Tin (Sn)	Smelting/Refining	200	3.2	Classen et al 2009
Iron (Fe)	Pig Iron / Blast Furnace	21.491	2.3	Kellogg 1974
Molybdenum (Mo)	Roasting	175	N/A	Landfield Greig 2008
Gases				
Argon (Ar)	Air separation / Cryogenic distil.	0.37	N/A	Agrawal et al 1989
Hydrogen (H ₂)	Steam reforming	1.14	10.4	Dufour et al 2009
	Water electrolysis (Grid/Wind)	160-220	1.86-0.9	Dufour et al 2009
	Thermal cracking	74.54	2.23	Dufour et al 2009
Other consumables				
Sodium hydroxide	Chloralkali Electrolysis	21	1.2	Bousted 2005

Table 2 - Inventories for the manufacturing process.

Process	Major inputs/outputs	Value	Functional Units	References
Gas Atomisation	Ni-Al (+dopant Fe, Mo, Sn, Cr) melt alloy	1	kg	Calculated
	Electrical energy to melt (+200 °C superheat)	0.7-0.8	kWh/kg Ni-Al	Yule and Dunkley 1994

	Argon	0.333	kg/ kg Ni-Al	Agrawal et al 1989
	Yield of 100µm powder	95%	of Ni-Al alloy	
	Ni-Al losses (collected dry cyclone filter)	0.01%	of Ni-Al alloy	
	Output: Ni-Al 100µm powder	0.95	kg/kg Ni-Al	
Cast and Crush	Electrical energy to melt (+200 °C superheat)	0.7-0.8	kWh/kg Ni-Al	Calculated
	Electrical energy Crushing (1m-2cm)	0.001	kWh/kg Ni-Al	Pourghahramani 2006
	Electrical energy Grinding (2cm-200µm)	0.01	kWh/kg Ni-Al	Pourghahramani 2006
	Electrical energy Milling (200µm-10µm)	0.033	kWh/kg Ni-Al	Pourghahramani 2006
	Yield of 100µm powder	100%	of Ni-Al alloy	
	Ni-Al losses (collected filters)	0.01%	of Ni-Al alloy	Estimated
	Output: Ni-Al 100µm powder	0.99	kg/ kg Ni-Al	Calculated
Caustic Leaching	Ni-Al 100µm powder	1	kg	
	NaOH (20-30wt.% Sodium Hydroxide)	3-4.5	kg/kg Ni-Al powder	Devred et al 2009
	Distilled water for leaching	15	l/kg Ni-Al powder	Devred et al 2009
	Electrical energy for heating 3 hours at 80°C	0	kWh/kg Ni-Al powder	Exothermic
	Distilled water for storage	50	l/kg Ni-Al powder	Devred et al 2009
	Output: Sponge-Nickel (Dry)	0.5-0.3	kg/kg Ni-Al powder	Calculated

Table 3 – Activity and energy saving for different compositions of sponge nickel alloys (Ni in balance). Note activity has been normalised to the activity of the standard industry catalyst (SP-Norm).

System reference label	Aluminium content of master alloy (atomic %)	Dopant Fe, Mo, Sn or Ti (atomic %)	Normalised activity	Residence time decrease (min)	Energy saving (kWh/t-butanol)	Note
SP-norm	68.5	0	-	-	-	CC Industry standard catalyst
SP-GA1	68.5	0	2	10	11	GA powder <i>no</i> dopant
SP-GA2	72.5	0	2	10	11	GA powder <i>no</i> dopant
SP-GA3	75.0	0	6	20	23	GA powder <i>no</i> dopant
SP-GA4	77.5	0	7	25	29	GA powder <i>no</i> dopant
SP-GA5	80.0	0	4	15	17	GA powder <i>no</i> dopant
SP-GA6	75.0	1.5	13	60	70	GA powder dopant
SP-GA7	75.0	3.5	19	65	75	GA powder dopant

Figure Captions

Fig. 1 SEM images of nickel-aluminide powder produced by (a) the Cast and Crush (CC) and (b) Gas Atomisation (GA) methods.

Fig. 2 Overview of the LCA processes for the production and use of sponge nickel.

Fig. 3 (a) Overall process and system boundaries for the complete lifecycle of sponge nickel with further details of (b) Primary materials production phase and (c) manufacturing phase (Gas Atomised or Cast and Crush methods) for sponge nickel.

Fig. 4 Schematic outlining the components of a typical phase hydrogenation reactor.

Fig. 5 Predicted life cycle energy of sponge nickel used in a hydrogenation reactor.

Fig. 6 Total manufacturing Global Warming Potential (GWP) for selected sponge nickel catalysts (based on a BUWAL North American Energy mix).

Fig. 7 (a) Impact categories for all processes of sponge nickel production and (b) relative contributions by process across the impact categories.

Fig. 8 Total life cycle energy as a function of catalyst lifetime.

Fig. 9 Total life cycle Global Warming Potential (GWP) for the selected sponge nickel compositions (100 batches) where *SP-NORM* - Cast and Crush (CC) Industry Standard 68.5 atomic % Al master alloy (MA); *SP-GA1* (Gas Atomised (GA) 68.5 atomic % Al (MA); *SP-GA2* – GA 72.5 atomic % Al (MA); *SP-GA3* – GA 75 atomic % Al (MA); *SP-GA4* – GA 77.5 atomic % Al (MA); *SP-GA5* – GA 80 atomic % Al (MA); *SP-GA6* – GA 75 atomic % Al (MA), 1.5 atomic % dopant; *SP-GA6* – GA 75 atomic % Al (MA), 3.5 atomic % dopant.

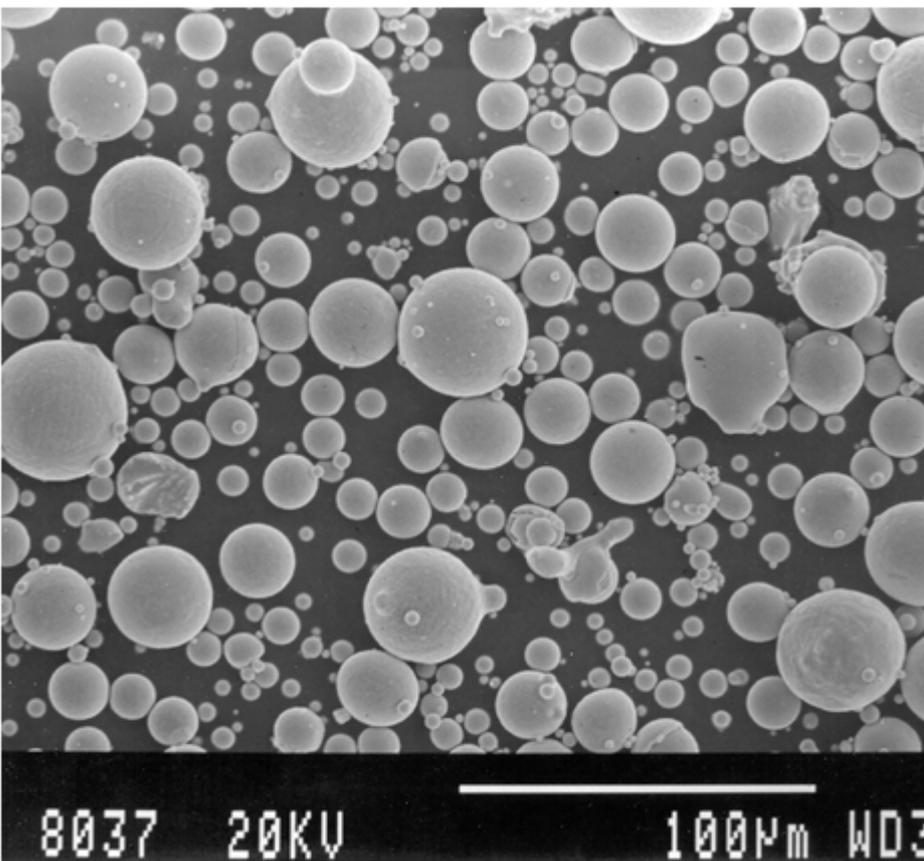
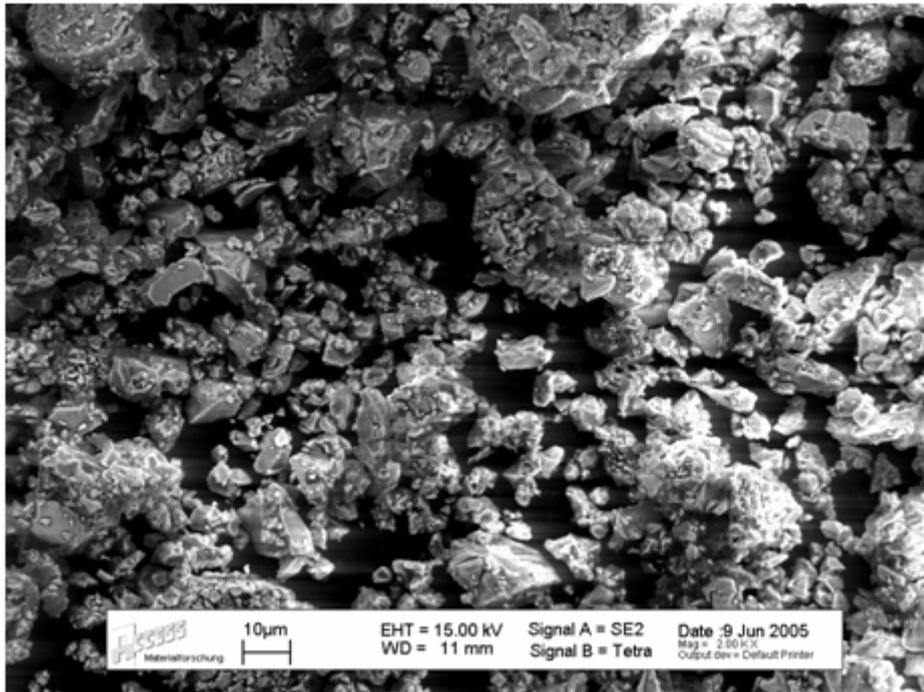


Fig. 1

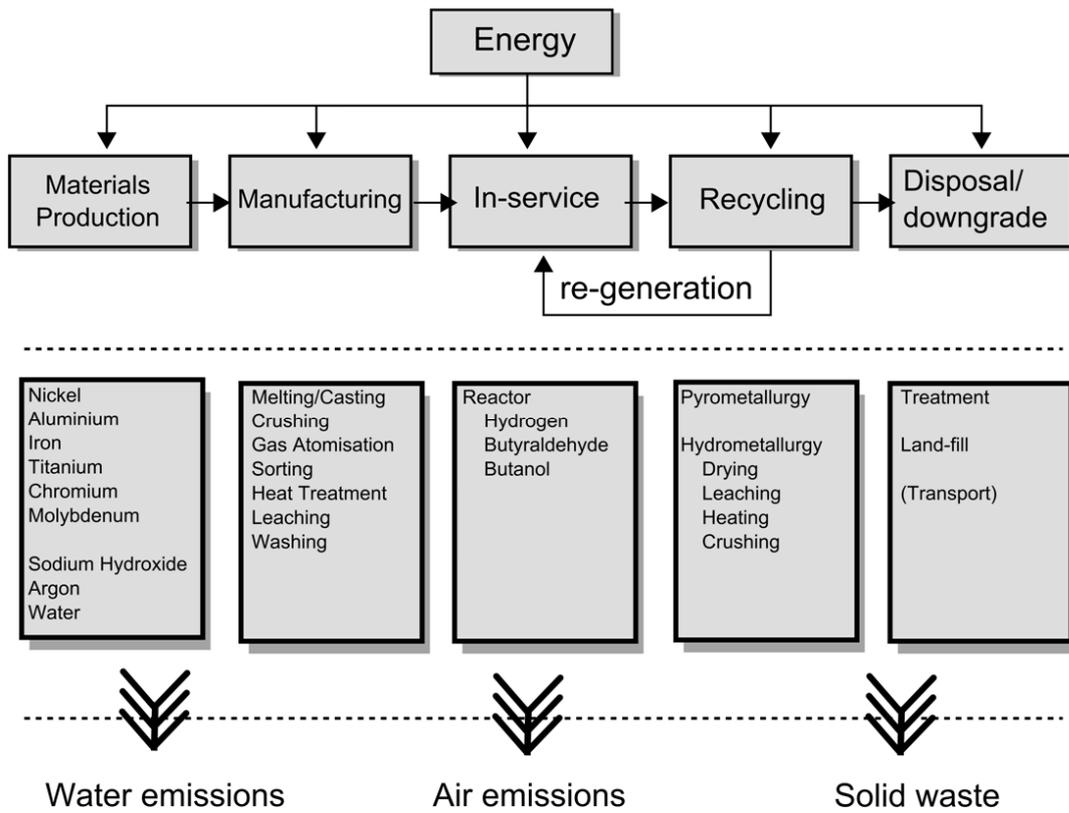
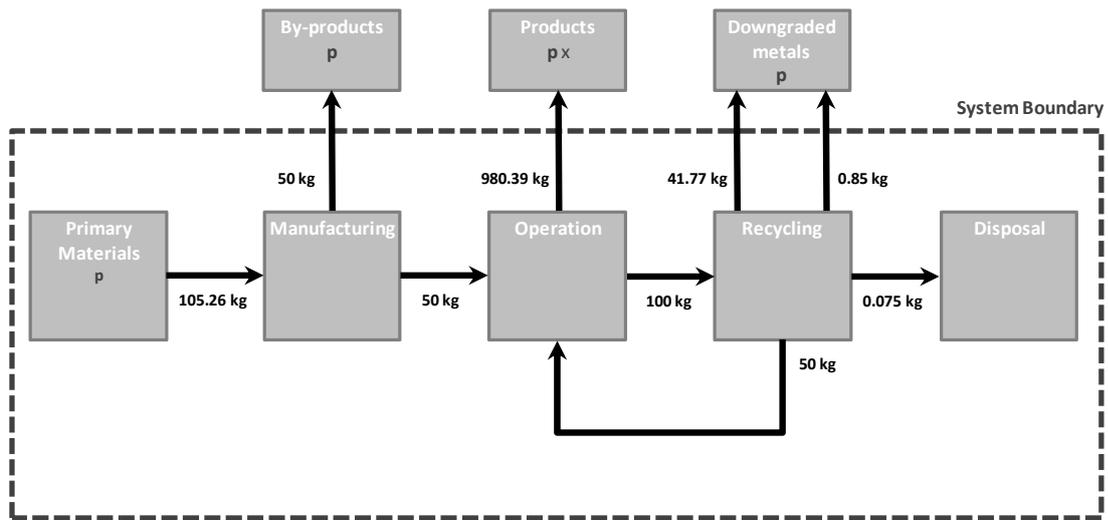
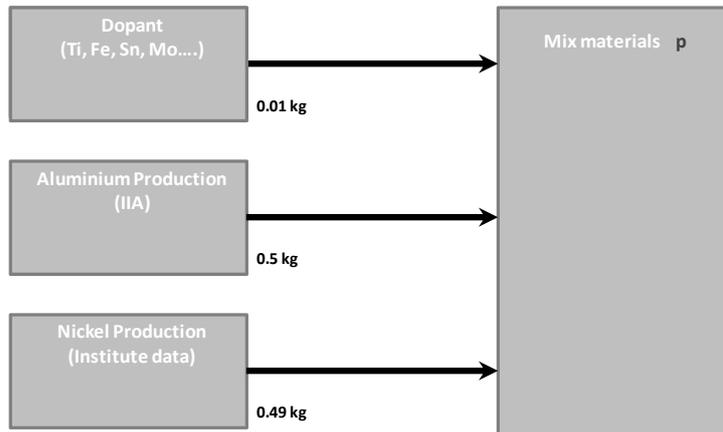


Fig. 2

(a) Sponge Nickel (Complete lifecycle)



(b) Primary materials p



(c) Manufacturing

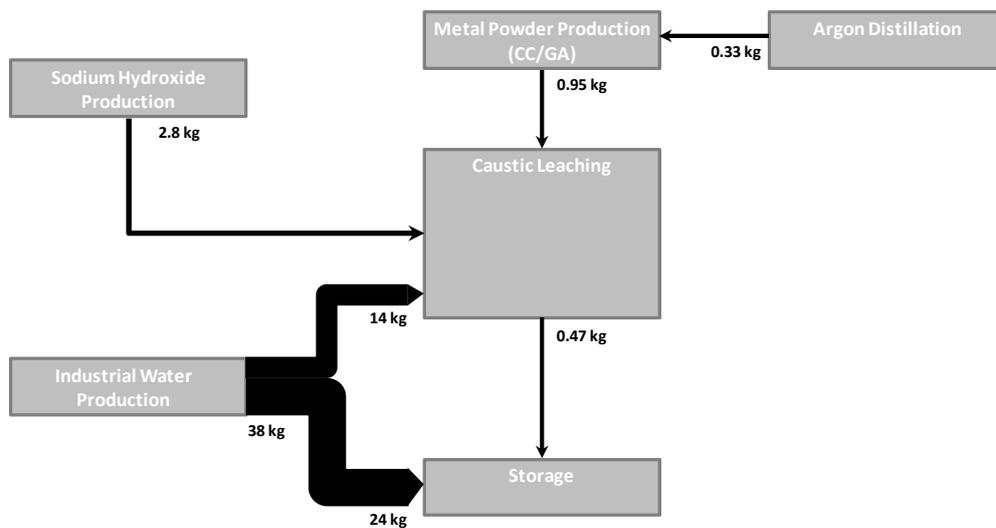


Fig. 3

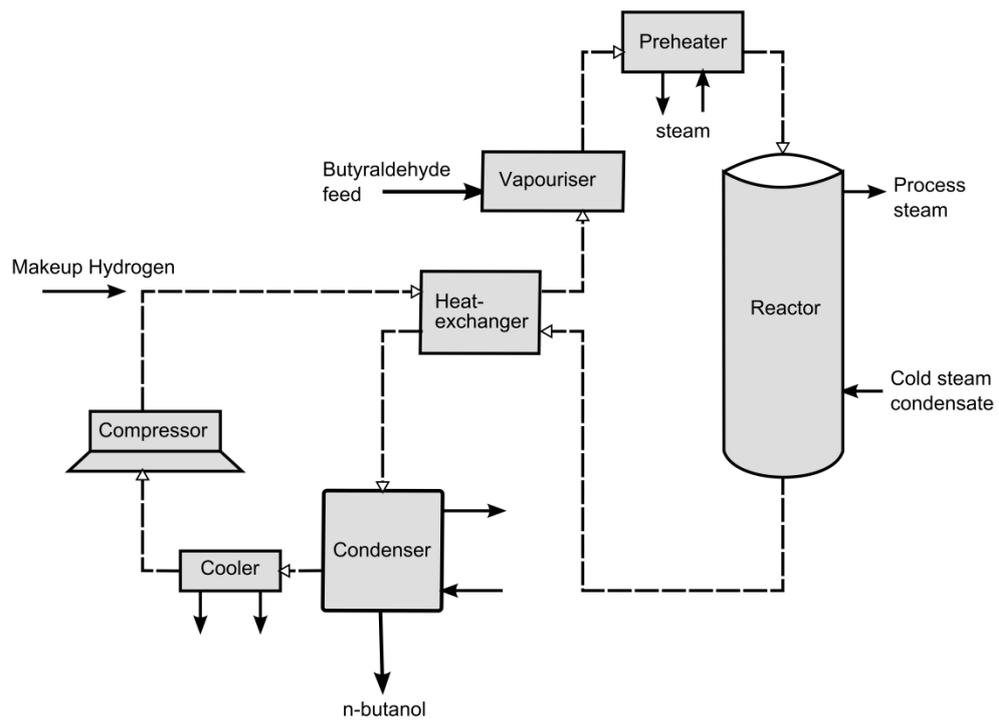


Fig. 4

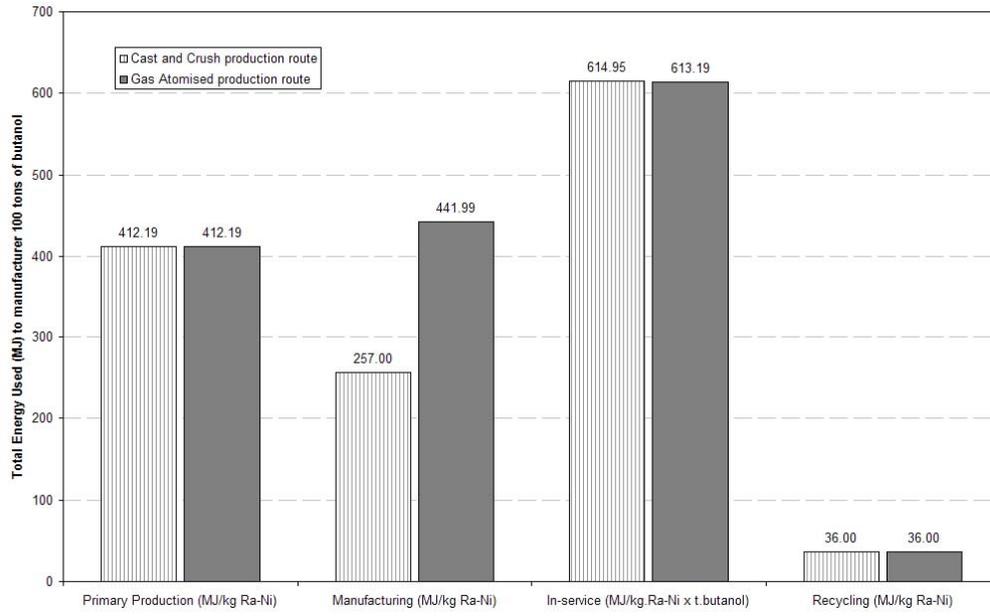


Fig. 5

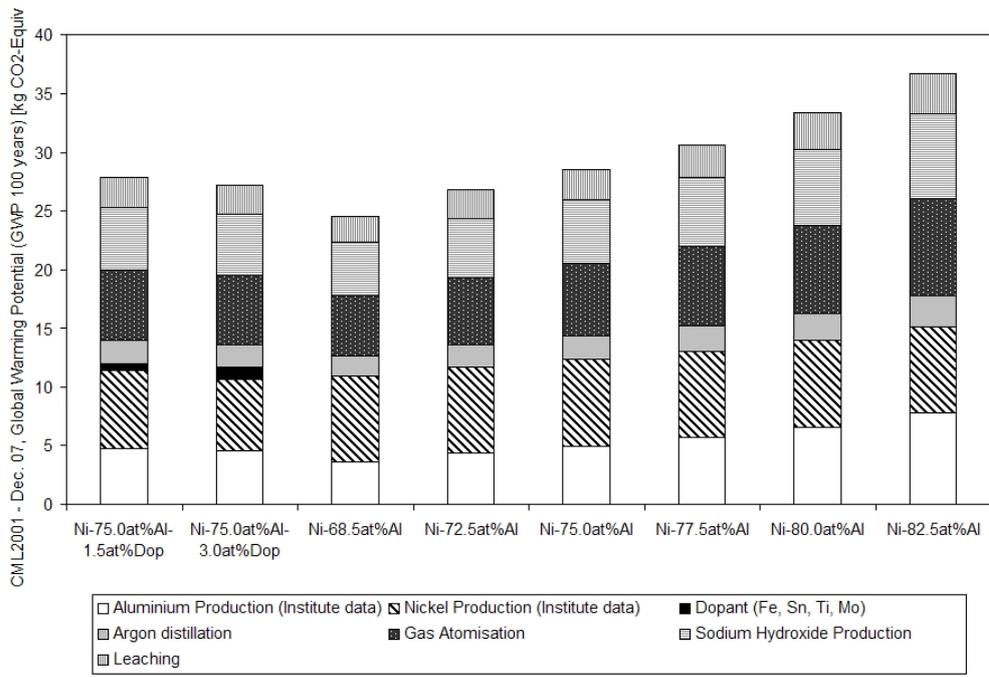
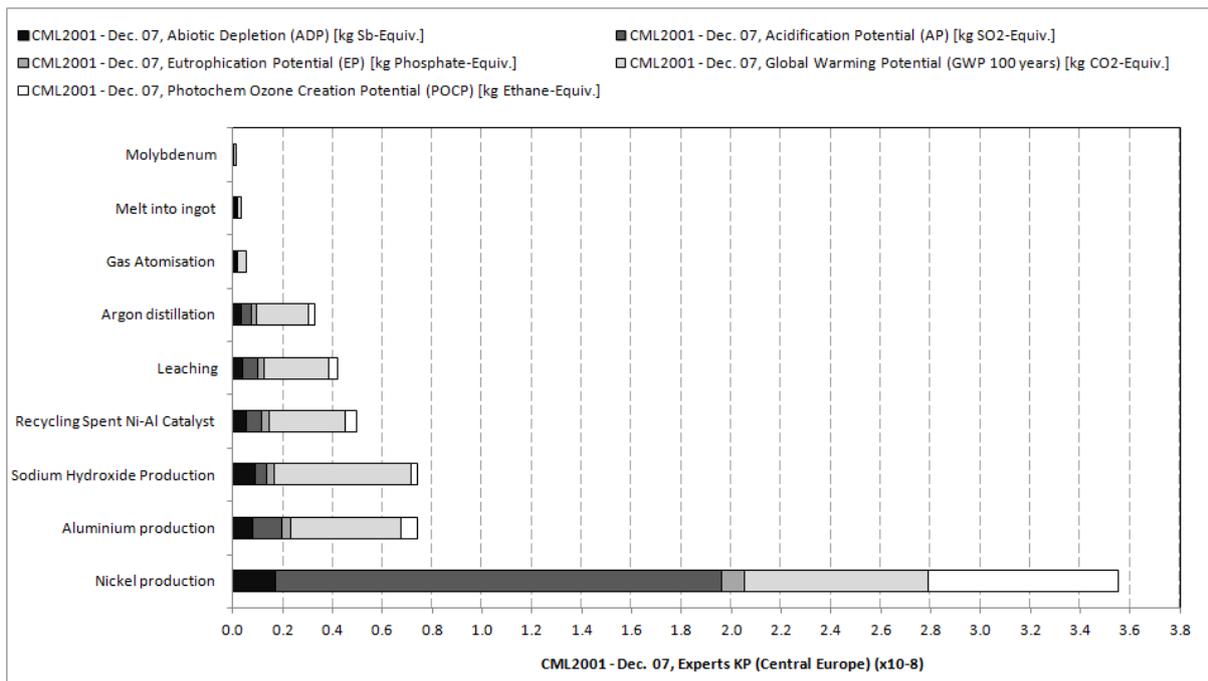


Fig. 6

(a)



(b)

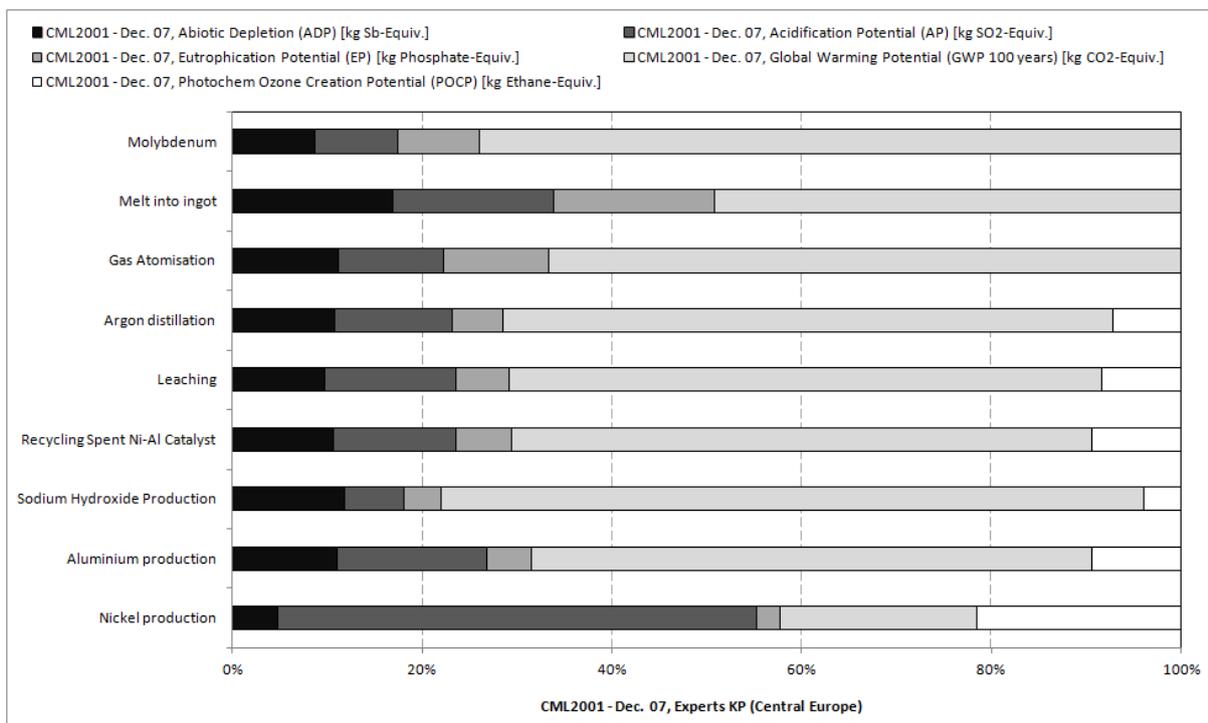


Fig. 7

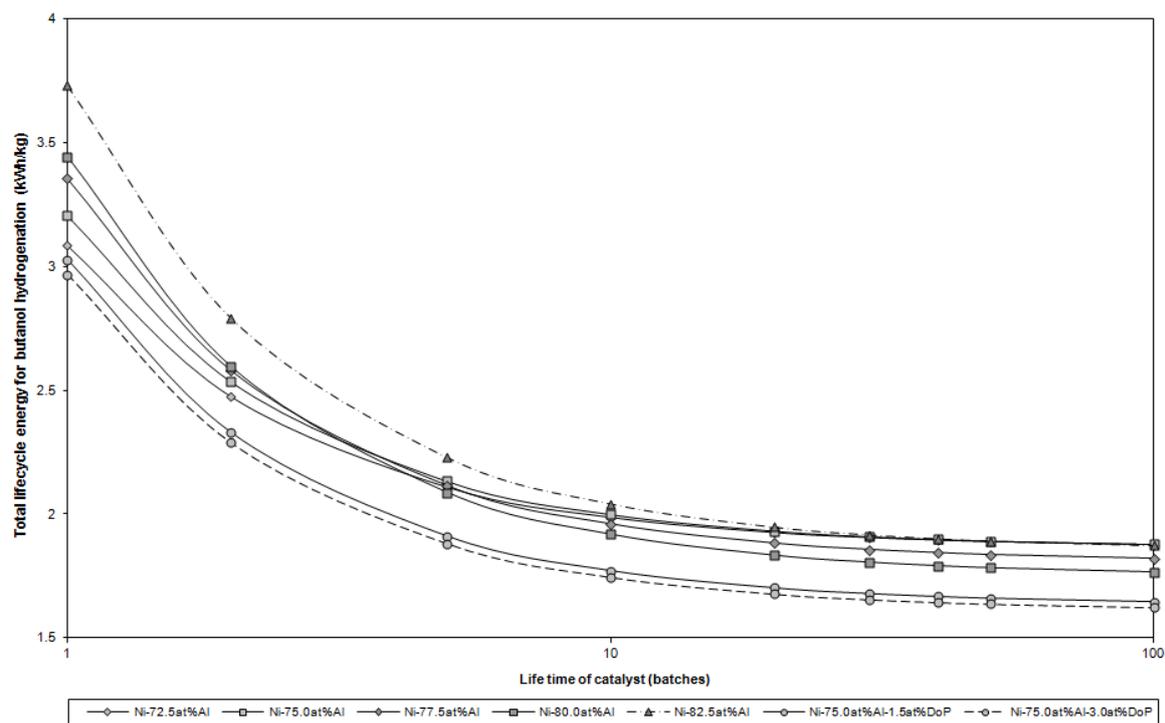


Fig. 8

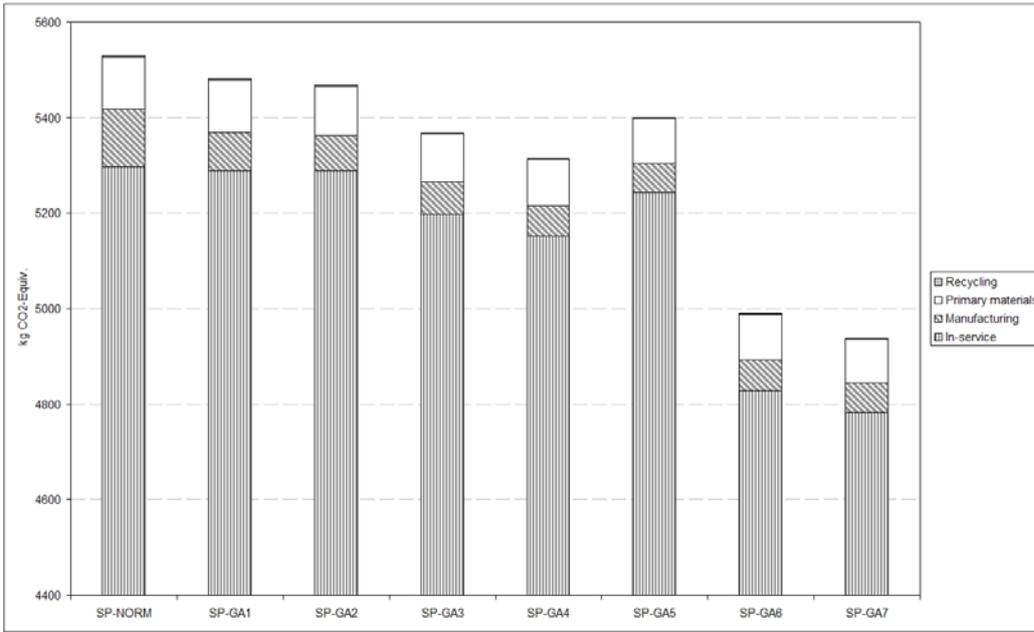


Fig. 9