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# ABSTRACT

# INTRODUCTION

Biomass gasification is an energy route to second generation fuel. Gasification process involves heating substances that are rich in carbon in the presence of steam and/or oxygen/air. The product from this process includes synthesis gas, which is a gaseous fuel of low to medium heating value (P. Mondal, G.S. Dang, & M.O. Garg, 2011).

However biomass gasification derived synthesis gas is known to have a number of contaminants which include particulate matter, tars (condensable hydrocarbons), sulphur compounds, nitrogen compounds, alkali metals i.e. potassium and sodium, and chlorine (J. Woolcok & C. Brown, 2013). The amounts of contaminants produced depend on the feedstock used as well as the type of gasifier technology used to produce the synthesis gas.

These contaminants are potential problems to downstream processes. Potential downstream processes such as gas turbines in heat and power generation, methanol synthesis, fischer-tropsch synthesis and fuel cells have strict requirements in terms of quality of fuel needed. These contaminants each have specific problems to downstream processes such as blocking of pipelines, corrosion, poisoning and deactivation of catalysts. It is then necessary to clean the synthesis gas before use in downstream applications.

The gas clean-up technologies are generally classified according to the temperatures of operation although there are no clearly set guidelines for their classification (J. Woolcok & C. Brown, 2013). Cold gas clean-up technologies include the use of liquid adsorbents. These technologies have high efficiency and are technically proven to be reliable however the low temperatures required for these clean-up technologies introduce a low thermal efficiency to the plant. The gas has to be cooled before removing contaminants and then reheated for the downstream processes. This makes hot gas cleaning highly advantageous and desirable. The challenge with hot gas cleaning is obtaining materials that can withstand high temperatures.

# WHY BIOMASS GASIFICATION

The synthesis gas (mainly composed of hydrogen, H2 and carbon monoxide, CO) is the main product of biomass gasification and it has a number of uses in today’s world. In a brief summary, the gas can be used to provide process heat, generate electric power, further processed into transportation fuels via the fischer-tropsch method as well as synthesized into important, high-value chemicals such as ammonia and methanol. Figure 1 below shows a summary of the various syngas conversion routes.

**Fig 1: Synthesis gas conversion routes (P.L. Spath & D.C. Dayton, 2003)**

However, the current use of fossil fuels, for example in the production of heat, electricity, transportation fuels has a negative side effect to the global climate. Combustion of the fuels releases carbon dioxide, CO2 which is a greenhouse gas that is known to greatly contribute to global warming. The National Aeronautics and Space Administration, (NASA) reports an average temperature increase of 0.80C from 1880 (NASA). Today, fossil fuels are a major source of the global energy and will still have >50% dominance in the power sector in 2035 (Agency, 2013 Key world energy statistics, 2013). This shows how critical it is to find an alternative energy source that has no CO2 emissions or is CO2-neutral. Figure 2 shows a continuing rise in emission of CO2 from fossil fuels.



**Fig2: CO2 emissions by fuel (Mt of CO2) (Agency, 2013 Key world energy statistics, 2013)**

The global climate change hence has had an impact on the search for unconventional energy resources. A requirement for the alternative energy source to replace the fossil fuels is that it must have high heating values and minimum greenhouse gas emissions.

Biomass is considered to be CO2-neutral although its use should not compete with the food market or affect the use of the environment. It is considered CO2-neutral because the CO2 that is removed from the atmosphere by the biomass is released in the same form during gasification with no net increase in the atmosphere within the natural biogenic carbon cycle time (Curran, 2012).

Biomass has an additional advantage over the fossil fuels being that it is a renewable energy source. Wood has been used as an energy source since the remote ages. It still fills a major portion of Africa’s energy need as it is processed into charcoal for domestic heat supply. Development of technology to go beyond charcoal production from biomass into transportation fuel and heat and power production on an industrial scale shows the urgent need in finding alternative energy sources over diminishing fossil fuels.

The international energy agency reports that a 25% rise in fossil fuel demand is expected by 2035 and yet fossil fuels are in limited amounts (Agency, World Energy Outlook 2011, 2011). There is great debate about when the peak oil will occur due to the heavy global reliance on oil and the need to find an alternative and convenient energy resource to replace it. Geology should be able to report how much oil is left but this is affected by a number of factors such as supply and demand and the advancement of technology in oil extraction (Graefe, 2009). A white paper prepared by the Colorado rviver commission of Nevada on world fossil fuel reserves and projected depletion in 2002 shows that they years of reserves left are 98 for petroleum, 166 for natural gas and 230 for coal (nevada, 2002).

Research and development of technology to convert biomass into fuel has also been driven by economic and national security (V. Singh & Harvey, 2009). Biomass compared to fossil fuels, are more evenly distributed. Using biomass as an energy source would reduce the reliance of nations on fossil fuel imports and hence the possibility of the major fossil fuel energy suppliers to use their energy resources as a way to attain their strategic and/or political targets. The increasing cost of oil may also make biomass-based fuel cheaper and more competitive.

# GASIFIER TECHNOLOGY

The overall gasification process is comprised of different chemical reactions. The major chemical reactions that occur during the gasification process include partial oxidation (reaction with oxygen), Boudouard reaction (reaction with CO2), steam gasification (reaction with steam), pyrolysis (thermal decomposition in absence of oxygen), water-gas shift reaction and methanation (P. Mondal, G.S. Dang, & M.O. Garg, 2011). Combustion is an unwanted chemical reaction in gasification because it yields product gas with no residual heating value i.e. CO2 and H2O (Higman & van der Burgt, 2008). A summary of the chemical reactions during gasification of cellulose can be seen in table 4.

The gas produced, synthesis gas technically consists of only hydrogen and carbon monoxide gas but the term is used in the industry to refer to the gaseous products from gasification processes (J. Woolcok & C. Brown, 2013). Other gaseous products produced include carbon dioxide, CO2 methane, CH4, water vapor and trace impurities.

According to literature, there are different types of gasification reactors which can be broadly classified into 4 types depending on the flow of the biomass feedstock and the oxidant, method of support of the biomass in the gasifier reactor, and how heat is supplied to the reactor (P.Ciferno & J. Marano, 2002). Table 2 shows a summarized table of the classification according to the aforementioned factors.

**Table 2: Classification of gasifiers (P.Ciferno & J. Marano, 2002)**

|  |  |  |  |
| --- | --- | --- | --- |
| **Gasifier Type** | **Flow Direction**Biomass feedstock Oxidant | **Biomass support in Gasifier** | **Heat source** |
| Updraft fixed bed | Down | Up | Grate | Combustion of char |
| Downdraft fixed bed | Down | Down | Grate | Partial combustion of volatiles |
| Bubbling fluidized bed | Up | Up | None | Partial combustion of volatiles and char |
| Circulating fluidized bed | Up | Up | None | Partial combustion of volatiles and char |

The fixed bed gasifiers have a well proven technology that is low cost and simple. The biomass is supported by a grate and the depth of the biomass bed is kept constant by adding the biomass from the top of gasifier reactor. The particle size of the feedstock is in the range of 2-50 nm. Commercial fixed bed reactors include the Lurgi gasifier.

**The updraft fixed bed reactor** has the oxidant (air or Oxygen and/or steam) introduced from the bottom of the grate and passed through the bed of biomass. Complete combustion occurs at the bottom of the reactor bed to give CO2 and H2O at a temperature of approximately 10000C. As the hot gases diffuse upward though the bed, they are reduced to H2 and CO. As the reduced hot gases move further up the reactor bed, they pyrolyse the biomass as it is slowly moves to the bottom of the reactor. The biomass is preheated and dried by the hot gas as it exits the reactor at temperatures of approximately 5000C. These reactors have high energy efficiency that allows the gasifier to be used with feedstocks that have high moisture content. The disadvantage is the large amounts of tar that are produced and released with the syngas.

**The downdraft fixed bed Gasifier** has a similar set-up to the updraft fixed bed gasifier but with the oxidant fed from the top of the gasifier down to the reactor together with the biomass feedstock. The gases react with char as they flow downwards at temperatures of approximately 800-12000C and form CO and H2. Since most of the tar that is formed is combusted minimal tar clean-up is required compared to the updraft reactor. The system however requires feed with low moisture content. *The combustion zone is usually in the range of 1,300 to 1,8000C and the synthesis gas exits at typical temperatures of approximately 5000C while the operating pressure range is 0.15-2.45MPa (P. Mondal, G.S. Dang, & M.O. Garg, 2011). The ash that is formed in fixed bed gasifiers exits from the bottom.*

The fluidized bed gasifiers have a bed of inert solid materials such as sand that are fluidized by the oxidant with the feedstock. The feedstock and oxidant introduced from the bottom of the reactor. This mixing allows for a constant temperature distribution in the gasifier. The feed particle size is about 8nm (ref).

**The Bubbling Fluidized bed Gasifier** has the oxidant forced through the fine inert particles at minimum fluidization velocity where the gas ‘bubbles’ through the media. **The Circulating Fluidized bed gasifier** has higher velocities than the minimum fluidization point and the particles are entrained in the gas stream. The particles and the gas exit the reactors from the top and the particles are separated from the gas in a cyclone and put back into the reactor. These gasifiers exhibit high conversion rates with a low yield of tar and char.

The differences between these gasifier designs lie in the ease of up scaling, thermal efficiency and tar yield (ref). The fixed bed reactors cannot easily be scaled up due to the limitation of penetration of air through the large biomass beds.

It is important to note that biomass gasification is not the only route to synthesis gas production. Other routes include steam reforming of natural gas and coal gasification with steam reforming of natural gas being the most economic technology (ref).

# BIOMASS FEEDSTOCKS

Biomass feedstock is a complex organic feed that comes from recently living material. They include trees, agricultural crops, and forests. The complexity of the feed comes from the varying chemical composition among the different plants and species. The lack of homogeneity pose a problem to the gasifiers that are designed to handle a consistent biomass feedstock composition. Table 3 looks at the proximate and ultimate analyses of potential gasifier feedstocks and Table 4 shows a summary of important chemical reactions of selected cellulose during gasification.

The common factor however is high moisture and oxygen content added to a similar fibrous structure composed of cellulose, hemicellulose and lignin. The high oxygen and moisture content lead to production of a lower heating value synthesis gas product compared to other synthesis gas precursors such as natural gas and coal.

**Table 3: Proximate and ultimate analysis obtained from ECN Phyllis2 database (Netherlands)**

|  |  |  |
| --- | --- | --- |
| **Fuel** | **Proximate analysis** | **Ultimate analysis wt% (daf)** |
|  | **Moisture wt% (ar)\*** | **Ash wt% (dry)** | **Volatile matter wt% (daf)\*\*** | **C** | **H** | **O** | **N** | **S** |
| **Coal** | 7.93 | 10.85 | 39.97 | 78.83 | 5.07 | 14.00 | 1.55 | 1.46 |
| **Straw** | 14.24 | 7.55 | 81.30 | 48.46 | 5.97 | 43.65 | 0.87 | 0.16 |
| **Treated wood** | 15.21 | 5.76 | 80.61 | 51.37 | 6.11 | 41.13 | 1.06 | 0.11 |
| **Untreated wood** | 17.25 | 2.25 | 82.07 | 50.71 | 6.08 | 42.84 | 0.38 | 0.06 |
| **Grass/Plants** | 30.90 | 7.27 | 82.65 | 49.02 | 6.14 | 43.49 | 1.31 | 0.17 |
| **Paper** | 7.56 | 9.99 | 90.31 | 46.61 | 6.39 | 46.09 | 0.31 | 0.10 |
| **Bagasse** | 19.02 | 5.79 | 83.38 | 48.95 | 6.11 | 44.35 | 0.64 | 0.11 |
| **Algae** | 17.25 | 2.25 | 82.07 | 50.71 | 6.08 | 42.84 | 0.38 | 0.06 |

\*ar – as received

\*\*daf – dry-ash-free

Note: ultimate analysis does not add up to exactly 100% due to presence of trace elements i.e. Chlorine

**Table 4: Reactions during gasification of selected cellulose (W. Huber, Iborra, & Corma, 2006)**

|  |  |  |
| --- | --- | --- |
| **Classification** | **Stoichiometry** | **Enthalpy (KJ/g.mol) ref temp. 300K** |
| Pyrolysis | C6H10O5 5CO + 5H2 + C | 180 |
|  | C6H10O5 5CO + CH4 + 3H2  | 300 |
|  | C6H10O5 3CO + CO2 + 2CH4 + H2 | -142 |
| Partial oxidation | C6H10O5 + ⅟2O2 6CO + 5H2 | 71 |
|  | C6H10O5 + O2 5CO + CO2 + 5H2 | -213 |
|  | C6H10O5 + 2O2 3CO + 3CO2 + 5H2 | -778 |
| Steam gasification | C6H10O5 + H2O 6CO + 6H2 | 310 |
|  | C6H10O5 + 3H2O 4CO + 2CO2 + 8H2 | 230 |
|  | C6H10O5 + 7H2O 6CO2 + 12H2 | 64 |
| Water-gas shift | CO + H2O CO2 + H2 | -41 |
| Methanation | CO + 3H2 CH4 + H2O | -206 |

# CONTAMINANTS FROM BIOMASS GASIFICATION

A general gasification process of carbonaceous material involves de-volatilization of the feedstock at temperatures ranging from 1000-15000C to give volatile hydrocarbons that further react to give syngas based on the following general chemical reaction (E. Shoko, B. McLellan, A.L. Dicks, & J.C. Diniz da Costa, 2006):

|  |
| --- |
| CHxOy + (1 – y)H2O ( $\frac{x}{2}+1-y)$H2 + CO |

In addition to the volatile hydrocarbons, a solid residue called char is formed. Valero et al. came up with a detailed formula for char as CHhOoNnSsZ which contains carbon, hydrogen, oxygen, nitrogen, sulphur and mineral matter which is represented by Z (Valero & Uso´n, 2006).

Similar to the chemical reactions of selected cellulose shown in table 4, below are the general chemical reaction equations that occur during gasification of CHhOoNnSsZ (E. Shoko, B. McLellan, A.L. Dicks, & J.C. Diniz da Costa, 2006):

|  |  |
| --- | --- |
| **Combustion** | CHAR + acO2 bcCO + ccCO2 + dcH2O + ecH2S + fcN2 |
| **Boudouard reaction** | CHAR + CO2 2CO + $\frac{o}{2}$H2O + $(\frac{h }{2}-s-o)$H2 + sH2S + $\frac{n}{2}$N2 |
| **Steam gasification** | CHAR + (1 - o)H2O CO + (1 – o + $\frac{h}{2}$ - s)H2 + sH2S + $\frac{n}{2}$N2 |
| **Reaction with H2 in absence of O2** | CHAR + $(2+o+s-\frac{h}{2})$H2 CH4 + oH2O + sH2S + $\frac{n}{2}$N2 |
| **Methanation** | CO + 3H2 CH4 + H2O |
| **Carbonyl Sulfide formation** | H2S + CO2 COS + H2O |
| **Water-gas shift** | CO + H2O CO2 + H2 |

The general chemical reactions show the production of some contaminants for downstream process in the synthesis gas such as H2S, COS and N2. Other important contaminants include particulate matter, condensable hydrocarbons and alkali metals mostly comprising potassium, K and sodium, Na (J. Woolcok & C. Brown, 2013).

This project report focuses on high temperature removal of sulphur as Hydrogen sulphide.

## SULPHUR AS A CONTAMINANT

Sulphur in the biomass feedstock is converted to H2S with lower amounts, to carbonyl sulfide (COS). Sulphur is known to cause poisoning of catalysts and corrosion in downstream processes. The presence of 1ppmv H2S in a Solid Oxide Fuel Cell (SOFC) with Ni/YSZ anode leads to a significant drop in performance of the fuel cell (P.V. Aravind & Wiebren de Jong, 2012).

Sulphur can be removed in-situ and/or downstream of the gasification process. In-situ methods include the use of minerals such as limestone and dolomite.Calcium carbonate reacts with hydrogen sulphide to give an unstable calcium sulphide, CaS product that reactswith oxygen in an un-wanted side reaction to give calcium sulphate. Calsium sulphate covers the surface of the sorbent reducing its efficiency in sulphur removal.

Downstream sulphur removal processes usually employ oxides of transition metals such as zinc, copper, nickel and manganese. However, a stable and reliable technology for removal of sulphur at temperatures over 6000C is yet to be developed.

# CHOICE OF CATALYST

Based on literature, the most promising and researched regenerative high temperature adsorbents for H2S removal include zinc, iron, manganese, copper and calcium (Cheah, L. Carpenter, & A. Magrini-Bair, 2009). Xiangmei, in her PhD on biomass gasification has summarized the advantages and disadvanteages of downstream sorbents in sulphut capture (Meng, 2012). In her summary, she mentions that ZnO sorbents have the most favourable thermodynamic property in H2S removal however it is easily vaporized at high temperatures (approximately 6000C) while manganese oxide possessed a better combination of desired high temperature sorbent materials.

The criteria for high temperature adsorbent for sulphur removal include having high sulphur adsorption capacity, fast adsorption kinetics, high temperature stability and resist being reduced in reducing environments. It must also be easily regenerable without loss of its sulphur adsorption capacity (Cheah, L. Carpenter, & A. Magrini-Bair, 2009). Manganese oxide, MnO has been a regular choice among research groups.

Manganese oxide is reported to exhibit high sulphur removal capacity at temperatures above 6000C with a fast reaction rate as well as show great stability during in sulfidation-regeneration cycles (Ren, Bao, Li, Chang, & Xie, 2010). Manganese oxide does not easily reduce to its elemental form which is an advantage the oxide holds over oxides such as Zinc and Copper oxide which have a higher reaction rate under similar conditions (Cheah, L. Carpenter, & A. Magrini-Bair, 2009).

Wakker et al. developed a process that uses MnO or FeO to removal of H2S and COS at 400-8000C (Wakker, W. Gerritsen, & A. Moulijn, 1993). The catalyst was subjected to more than 300 cycles of sulfidation-reaction, with deactivation only noticed within the first 10 cycles.

 Bakker et al. also report to have developed a MnO based adsorbent with an optimum adsorbent capacity realized between 800-9000C (J.W. Bakker, Kapteijn, & A. Moulijn, 2003). H2S concentrations were reduced from 6400ppm to less than 50ppm.

The general adsorption and regeneration reactions for MnO and H2S are shown below.

**Sulfiding:**

|  |
| --- |
| MnO + H2S MnS + H2O  |

**Regeneration:**

|  |
| --- |
| MnS + 3/2 O2  MO + SO2 |

The SO2 produced can be sent to a Claus process for removal as elemental suplhur or to a sulphuric acid production unit.

The potential disadvantage of using MnO is the formation manganese sulphate which requires very high temperatures (>4500C) of sorbent regeneration. The sulphate leads to fracturing of the catalyst particles because the sulphate leads to volume expansion of the sorbent (Bakker, 1998).

* Each of the for the syngas determine the level of syngas purification that will be needed.
* Sulfidation mechanism?

## LITERATURE REVIEW

Table 5 shows a summary of sulfidation and regeneration conditions for manganese oxide based sorbents from selected publications listed in a journal article by Cheah at al. and references there-in (Cheah, L. Carpenter, & A. Magrini-Bair, 2009).

**Table 5: sorbernt materials, sulfidation and regeneration condition from Cheah et al. and references there-in (Cheah, L. Carpenter, & A. Magrini-Bair, 2009)**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Refs | Materials | Sulfidation conditions | Outlet H2S concentration | Cycles | Conditions for regeneration |
| Wakker et al. (1993) | MnO or FeO on ɤ-Alumina | 400-8000C,0 - 1% H2S,0 – 1% COS | 0 – 100ppm | 10 - >300  | in gas containing steam |
| Ben-Slimane and Hepworth (1995) | MnO on ɤ-Al2O3/TiO2 | 700 - 10000C,3% H2S in mix | Approx.. 200ppm | 25  | air at 9000C |
| Gasper-Galvin et al. (1998) | Cu/Mo/Mn on Zeolite | 8710C, 0.2% H2S in mix, 1% CH4, 19% H2O | < 10 – 100ppm | 5  | 50/50 air and steam at 8710C |
| Bakker et al. (2003) | MnO + ɤ-Al2O3 | 400 - 10000C, 1.0% H2S in H2/Ar | < 5ppm | 110  | 30% SO2/ 50% H2O/ 20% Ar at 8500C |
| Yoon et al. (2004) | Mn ore (β-MnO2) | 550 - 8500C, 1% H2S in mix | < 1ppm | 20 | 4% O2/N2 at 550 - 8500C or 4% O2/N2 + 0.5% NH3 + 5-20% H2O followed by CO/H2/CO2/N2 reduction |

# EXPERIMENTAL METHODS

## SUPPORTED CATALYST PREPARATION

Impregnation involves adding a solution containing the required metal onto a porous catalyst support. Anderson and Garcia in their book, ‘Supported metals in catalysis’, describe three processes that occur during impregnation (A. Anderson & Garcia, 2005). The first process involves transport of the solute to the pores of the support followed by internal diffusion within the pores and then up-take of the solute by the pore wall.

The metal-containing solution is made by dissolving the active metal precursor in an aqueous solution or an organic solution. The volume of the solution used is equal to the pore volume of the porous support. This volume can be determined by titration method. The liquid used to dissolve the active metal precursor is slowly added to the porous powder support until the powder does not flow freely and becomes sticky. This happens when the liquid has filled the pores of the solid powder. Adding more liquid to this would make the solid powder become wet and seem to flow like mud.

The maximum metal loading on the catalyst support is determined by the solubility of the metal precursor in the pore volume. If a higher loading than the solubility is needed, successive impregnations (and heat treatments) can be done.

The catalyst MnO supported on ɤ-Al2O3 was prepared using the incipient wetness impregnation method. The catalyst was chosen because it was developed to remove H2S and COS from gases produced from coal gasification at high temperatures ranging from 401.85-801.85oC (Wakker, W. Gerritsen, & A. Moulijn, 1993). The method used here is similar.

Two catalysts were prepared from different metal precursors: Manganese (ll) acetate tetrahydrate, (C4H6MnO4.4H2O >99%, Aldrich) and Manganese (ll) nitrate tetrahydrate (Mn(NO3)2.4H2O, Sigma-Aldrich) . The support used is Aluminium oxide (activated, neutral, gamma 96%, Strem chemicals).

First, the pore volume of the ɤ-Al2O3 support was determined. A known weight of the support (~ 0.5g) was placed onto a small glass container. Water was added to the support using a burette (10 ml) until the powder became sticky. This experiment was done twice.

To prepare the catalyst with a target loading of 7% Mn, the required amount of the metal precursor was dissolved in water of a volume equal to the pore volume of the mass of support to be used. The solution was then slowly added to the support.

The samples were left to dry overnight at room temperature and then calcined in static air at 300oC for 16hrs.

After calcination, the manganese is present as MnO2 or Mn2O3. The catalyst reduction is carried out at reaction temperature in the reactor.

Appendix A shows calculations used during preparation of the catalyst.

## X-RAY DIFFRACTION (XRD)

X-ray diffraction is based on the fundamental Braggs law equation which infers that the larger the structural size of a particle, the lower the scattering angle (Che & C. Vedrine, 2012) (S. M. Ashraf, Ahmad, & Riaz, 2008).

Braggs law: nλ = 2d sin θ

The equation shows the conditions required for constructive interference on incoming waves i.e. the relation between the wavelength, λ, interatomic distance, d, and the incident angle of x-ray, θ. Where n is the order of diffraction.

For crystalline catalysts, XRD is an important tool that enables structural studies, phase identification and quantitative phase analysis of the catalysts. The crystalline materials diffract the x-rays and the angles of diffraction are different for the different planes within the crystals. The diffraction pattern obtained are unique for a given compound or element.

The small (nano scale) particles give a “less than full destructive interfearance or signal cancellation of angels away from one of the Bragg conditions”. This gives broad diffraction peaks that are described by the Scherrer equation.

The Scherrer Equation: $\frac{kλ}{L cosθ}$

Where B = width at half-peak height of an XRD line
 L = size of the crystallites
 λ = X-ray wavelength
 θ = diffraction angle
 k = a constant usually equal to 1

The Scherrer equation shows the relation between the width of the peak at half peak height and the size of the crystallites.

XRD studies were carried out using the Bruker D( advance Davinci x-ray diffractomer between 5 and 75 degrees. The analysis was done on the ɤ-Al2O3 support and the two calcined catalysts prepared from manganese acetate precursor and manganese nitrate precursor.

## NITROGEN ADSORPTION

Nitrogen adsorption/desorption method is an important technique used in characterization of porous catalytic materials in order to determine their surface area, pore volume and pore size distribution. The nitrogen adsorption/desorption isotherms are determined over a range of relative pressures while allowing for slow equilibration (Sing, 2001). The adsorption isotherm is a plot of volume of gas adsorbed against relative pressure.

The Brunauer-Emmett-Teller (BET) equation shows the relationship between the volume of nitrogen adsorbed at a given partial pressure and the volume of nitrogen adsorbed at monolayer coverage ( S. Brunauer, PH. Emmett, & E. Teller, 1938).

The BET equation: $\frac{P}{V(Po-P)}=\frac{1}{Vm C} + \frac{\left(C-1\right)P}{Vm C Po}$

Where P = Partial pressure of Nitrogen

 Po = saturation pressure at the experimental temperature

 V = Volume adsorbed at P

 Vm = Volume adsorbed at monolayer coverage

 C = constant

The volume adsorbed at monolayer, Vm can be found by extrapolating the monolayer section to zero pressure.

The surface area, pore diameter, pore size distribution and pore volume were measured on the two catalysts prepared as well as the support. Measurements were carried out using the Micromeritics Tristar 3000 instrument.

A small amount of the samples were placed in sample tubes and degassed overnight at 2000C before being analysed. After degasification, the samples were cooled with liquid nitrogen to cryogenic temperatures. The adsorptive gas (Nitrogen) was introduced to the sample in successive amounts with carefully controlled increasing pressures to obtain the adsorption/desorption isotherms.

The surface area was determined as the BET surface area. The pore volume and pore size distribution were determined from the Nitrogen desorption curve using the Barret-oyner-Halenda (BJH) method.

## TEMPERATURE PROGRAMMED REDUCTION

TPR is catalyst characterization technique used to determine the temperature at which reduction occurs.

TPR measurements were carried out on the two calcined catalyst samples using the AMI-300 Altamira (BenchCAT 1000 Hp Hybrid) instrument. A small sample was placed in a U-shaped quartz reactor and placed in a furnace. A thermocouple is placed above the sample to record temperature measurements. A small plug of quartz wool was used to keep the sample in place. The calcined samples were first heated to 3500C at a rate of 100C/min while passing an inert gas (argon) at a rate of 50cc/min. This was done to desorb off species that are weakly adsorbed to the samples. Temperature programmed reduction measurements (TPR) were taken while heating the samples to 5500C at the same heating rate of 100C/min while passing a gas of 10% H2 in Argon at a flowrate of 50 cc/min. Hydrogen gas is consumed when reduction has occurred and the temperature at which this has occurred is detected by the Thermal conductivity detector (TCD).

# EXPERIMENTAL LAB SET-UP

MFC

MFC

MFC

MFC

MFC

N2 FLUSH

N2

H2S

O2

H2

Analysis

 vent

vent

 vent

Temperature

measurement

REDUCTION VALVE

REDUCTION VALVE

REDUCTION VALVE

REDUCTION VALVE

4-way

valve

3-way

valve

 By-pass

 oven

 Reactor

vent

N2

Aluminium blocks

H2SMIX

O2

H2

Figure 3: The lab set-up

The experimental lab set-up designed for analysis H2S removal by an adsorbate at high temperatures is shown in fig 3.

There are three gas lines from the gas distribution network connected to the lab setup supplying H2, O2 and N2. A fourth gas, 1% H2S in Argon is supplied through a gas cylinder that is placed within the lab set-up. A H2S detector is placed near the floor of the lab set-up to detect H2S leakage. The gas flowrates are controlled by bronkhorst mass flow controllers.

The reactor is a ceramic tubular reactor, 8.9mm internal diameter, 12.7mm outside diameter and a length of 750mm. A thermocouple is placed next to the reactor to measure temperature. Temperature control is by a eurotherm controller. An aluminium jacket is used to enclose the reactor in order to minimize heat loss. Heating is provided by an electrical heating source.

Analysis of the gaseous components from the reactor is done by a Pfeiffer quadrupole mass spectrometer.

The experimental lab set-up was not completed at the time of handing in the report. The challenges in completing the lab set-up include long delivery times for some spare parts that were required for the set-up. The current works that remain on the lab set-up include fixing a leakage at the capillary tube inlet to the mass spectrometer and changing a fitting that connects to the reactor since it could not be leak proof. The leak at the mass spectrometer inlet was detected while trying to calibrate the mass spectrometer.

A signed risk assessment copy of the lab-set up has been attached to the report as required.

## MASS FLOW CONTROLLER

Bronkhorst high tech mass flow controllers connected to 24Vdc power supply. They are designed for very low gas flowrates with a PID control and an electronically driven control valve. The maximum flowrate is 500 ml/min. The mass flow controllers require a pressure drop across the valve to work and the flowrate can be controlled by adjusting the valve opening which ranges from 0-100%. The valve opening is proportional to flow. Each of the flow meters is made specific for the corresponding gas it is to be used for. This is due to special requirements in materials required for the different gases.

The gas mass flow controllers were calibrated with their respective gases using the soap bubble meter method at flowrates that are expected to be used. The bubble meter technique measures volumetric gas flow rates and was used to examine accuracy of the mass flow controllers. A 100ml bubble meter was used to measure volumetric flow rates of each of the flow controllers with their respective gases. Appendix C shows the calibration curves obtained.

The system was leak tested and pressure tested prior to calibration to ensure reliable results with no loss of gases along the pipelines and for safety in regards to H2 and H2S. Appendix XX shows the procedures for Pressure test and leak test.

## TEMPERATURE CONTROLLER

The eurotherm temperature controller 2408 uses a PID control algorithm to give a stable control of the temperature (Eurotherm, 2007). It also includes an alarm system in case of deviation from the set-point.

## MASS SPECTROMETER

The instrument for analysis is a quadrupole mass spectrometer. A mass spectrometer is used to analyse gaseous chemical compositions using partial pressures measured under vacuum. Measuring the partial pressures of the different components requires separation of the gaseous mixture and then measuring the partial pressures in isolation. Gaseous mixture separation is done using the mass-to-charge ratio (m/e).

The gas is pumped to a low pressure vacuum chamber where it is ionized through electron bombardment. The electrons from the ion source (filament) collide with the gas particles and knock out electrons making them positively charged. The mass is measured by electric and/or magnetic field. The particles are them separated based on their mass-to-charge ratio by a mass filter.

The quadrupole mass filter is made up of 4 aligned rods which create an electric quadrupole field. A faraday detector and a secondary electron multiplier are used to measure the ion current which is a measure of the partial pressure of the gas molecules (Pfeiffer Vacuum GmbH, 2013). The quadrupole mass spectrometer operation and analysis software is called Quadera. It allows for simple operation of the mass spectrometer, reproducibility of the results and storage of relevant data.

# SULFIDING-REGENERATION PROCEDURE

The general sulfiding-regeneration cycle procedure for this research is a four-step procedure that can be briefly described as follows:

Sulfiding-flushing-regeneration-flushing

During sulfiding, the 1% H2S/Argon gas is passed over the catalyst where adsorption of the sulphur on the catalyst takes place.

|  |
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| MnO/ɤ-Al2O3 + H2S MnS + ɤ-Al2O3 + H2O |

The amount of H2S coming from the reactor is measured using a mass spectrometer. This is the amount of H2S that was not absorbed on the catalyst. The reaction proceeds until the concentration of H2S in the outlet gas is equal to the concentration entering the reactor. This is the adsorbent saturation point.

The system will then be flushed with N2 gas to remove the toxic H2S gas from the pipeline before regenerating the metal with O2 (or a mixture of O2 and N2).

|  |
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| MnS + ɤ-Al2O3 + 0.5O2 MnO/ɤ-Al2O3 + SO2 |

The system is then flushed again with N2 to remove O2 from the system and the cycle is repeated.

A breakthrough curve showing the concentration of H2S exiting the reactor as a function of time is obtained for each cycle.

# RESULTS

The catalysts were prepared with a target loading of 7wt% Mn on ɤ-Al2O3.

## XRD

Fig 4 shows superimposed XRD patterns obtained for unloaded ɤ-Al2O3 support and the impregnated support with MnO from acetate precursor and nitrate precursor.

The particle size for MnO/ ɤ-Al2O3 catalysts from acetate and nitrate precursors are estimated with the scherrer formula to be between ………and …………..nm.



**Fig 4: XRD patterns for unloaded ɤ-Al2O3 support, MnO/ɤ-Al2O3 catalyst from acetate precursor and nitrate precursor**

## NITROGEN ADSORPTION

Table 6 gives a summary of results obtained from the nitrogen adsorption (BET) test. The test was carried out on the fresh unloaded ɤ-Al2O3 support and the MnO impregnated samples from both the acetate precursor and nitrate precursor.

**Table 6: Physical parameters unloaded ɤ-Al2O3 support, MnO/ɤ-Al2O3 catalyst from acetate precursor and nitrate precursor**

|  |  |  |  |
| --- | --- | --- | --- |
| **Sample** | **BET surface area (m2/g)** | **BJH desorption pore volume (cm3/g)** | **BJH desorption average pore diameter (Å)** |
| **ɤ-Al2O3** | 205 | 0.322 | 44.73 |
| **MnO/ ɤ-Al2O3 from acetate** | 134 | 0.209 | 43.51 |
| **MnO/ ɤ-Al2O3 from nitrate** | 150 | 0.227 | 42.82 |

## TEMPERATURE PROGRAMMED REDUCTION

Temperature programmed reduction (TPR) studies were carried out on the catalysts that were prepared from different metal precursors. The results obtained as shown in fig 5a and 5b below.

**Fig 5a: TPR patterns obtained for MnO/ɤ-Al2O3 catalyst from acetate precursor**

****

**Fig 5b: TPR patterns obtained for MnO/ɤ-Al2O3 catalyst from nitrate precursors**

The TPR patterns for the MnO/ɤ-Al2O3 catalyst from acetate precursor and nitrate precursor.

Both samples show peaks between 250 and 5000C. From fig 5a, the the ex-acetate sample shows a reduction pattern that takes place over a broad temperature range (200-4500C). This is seen as broad and overlapping peaks. The major peak is located at around 3250C.

The ex-nitrate sample shows more pronounced peaks which represent a two-step reduction profile. The first and second peaks are seen at approximately 3750C and 4500C respectively.

# DISCUSSION & CHALLENGES

The results obtained from characterization of the two MnO/ɤ-Al2O3 catalysts prepared from acetate precursor and nitrate precursor show that the two catalysts are quite different. Their sulfur adsorption properties (activity) were not tested due to the challenges experienced with completing the lab set-up. The activity values can be compared to values in the literature to see how good the catalyst is.

However the characterization values have been compared with characterization values for similar catalysts that were found in literature. The catalysts were prepared with a target loading of 7wt% Mn and mostly compared with the XRD and TPR values reported by Kapteijn et al. Kapteijn et al prepared, among other loadings, a 6wt% Mn catalyst on ɤ-Al2O3 support (Kapteijn, et al., 1994). They suggest that the differences in characterization results between the ex-nitrate and ex-acetate catalysts is because the manganese oxide in alumina supported catalyst from nitrate is present as a micro-crystalline material, while from the acetate, it is present mostly as a surface metal oxide. This is in agreement with results obtained from the XRD pattern

Calcination at 3000C leaves manganese oxide present as the more thermodynamically stable MnO2 and Mn2O3 (Wakker, W. Gerritsen, & A. Moulijn, 1993). The two sharp peaks obtained in the TPR pattern for the ex-nitrate sample show a two-step reduction profile. In the first step, MnO2 and Mn2O3 are reduced to Mn3O4 which is then further reduced to MnO in the second step. The broad overlapping peaks seen from the ex-acetate sample suggest a highly dispersed catalyst with a one-step reduction profile. The Mn3+ is reduced to Mn2+ since a stable Mn3O4 cannot be formed at high dispersions (Kapteijn, et al., 1994).

# CONCLUSION

A regenerable high capacity manganese oxide on alumina catalyst has been prepared based on a procedure obtained from literature. Its adsorbent capacity even after subsequent regeneration has not been tested since the lab set-up was not complete to carry out such a test.

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# APPENDIX A: Calculations used in the preparation of the catalyst

Table showing results obtained from calculating pore volume

|  |  |  |
| --- | --- | --- |
| Weight (g) | Water volume (ml) | Pore volume (ml/g) |
| 0.5534 | 0.33 | 0.5963 |
| 0.5013 | 0.30 | 0.5984 |

Calculating the amount of salt needed to get 7% wt Mn:

For 1 gram of support:

For **Manganese Acetate** precursor:

Mass of Mn needed, mMn = mcat,total – mcat,support

 = $\frac{1}{1-0.07}$ – 1

 = 0.0753 g

Converting to number of moles, nMn = mMn/MMn

 = $\frac{0.075}{54.9}$

 = 0.001372 mol

Mass of manganese Acetate required, mC4H6MnO4.4H2O = $\frac{nMn}{MC4H6MnO4.4H2O}$

 = 0.001372 x 245.09

 = 0.3363 g

For **Manganese Nitrate** precursor:

Mass of Mn needed, mMn = mcat,total – mcat,support

 = $\frac{1}{1-0.07}$ – 1

 = 0.0753 g

Converting to number of moles, nMn = mMn/MMn

 = $\frac{0.075}{54.9}$

 = 0.001372 mol

Mass of manganese nitrate required, mMn(NO3)2.4H2O = $\frac{nMn}{MMn(NO3)2.4H2O }$

 = 0.001372 x 251.01

 = 0.344 g

Since both precursors have the same number of mols of water in them, and the number of Manganese mols is also the same, the calculation for the corrected volume of water that should be added will be the same:

For this, the pore volume for support calculated in Table X1 will be needed.

The pore volume,Vpore,support = 0.6ml/gram of ɤ-Al2O3 support

To get the corrected volume of water to be added, it is necessary to subtract the amount of water in the salt:

Nsaltwater = 4 x nMn

 = 4 x 0.001372

 = 0.005488 mol

Therefore, volume of water in the salt, Vsaltwater = $\frac{msaltwater}{rwater}$

 = $\frac{18 x 0.005488}{1}$

 = 0.09878 ml

Corrected volume of water to be used = Vpore,support - Vsaltwater

 = 0.6 – 0.09878

 = 0.50122 ml

# APPENDIX B: Leak test procedure

**Leak test procedure**

1. Close all outlets
2. Fill line with inert gas (i.e. N2) at moderate pressure (5-6 bars)
3. If all outlets are closed, the gas inlet flow should approach zero
4. Listen for any huge leaks (whistling sound?)
5. Check for small leaks with leak detection spray
6. Tighten nuts/joints where there are leakages
7. Pressurize and isolate equipment for some time (i.e. a few hours or leave it overnight). Check for any Pressure loss (Bar/h --> ml/min)
8. If everything seems ok, continue at a higher pressure and start over again.
9. If not ok, replace inert gas with H2 gas and use a CO detector to search for leaks
10. Ensure leak proof at operating conditions

Note:

Always leak test when the equipment has been modified (i.e. replaced parts, after reactor dismount/remount)

**Pressure Test**

1. Ensure all equipment used is certified for the operating conditions
2. Pressure testing should be carried out at higher pressure than desired operating conditions, at room temperature and with inert gas BUT REMEMBER Pressure tolerations are affected by temperature!
3. Close all outlets
4. Fill line with inert gas up to desired pressure

Note:

Always pressure test when the equipment has been modified (i.e. replaced parts, after reactor dismount/remount)

# APPENDIX C: Mass Flow Controller calibration curves

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Temp [K] | 295.35 |  |  |  |  |
| Trykk [torr] | 753.1 |  |  |  |  |
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|  |  |  |  |  |  |
| **Nitrogen MFC** | **Channel** | **4** |  |  |  |
|  | **Usertag** | **N2** |  |  |  |
|  | **Serial Number** | **SMN11211984B** |  |  |  |
|  |  |  |  |  |  |
| **Valve opening [%]** | **Volume [mL]** | **Time [s]** | **[mL/min]** | **(Corrected volume)** | **Corrected [mL/min]** |
| 40 | 9 | 2.44 | 221.3115 | 8.247945725 | 202.8183375 |
| 35 | 9 | 2.69 | 200.7435 | 8.247945725 | 183.9690496 |
| 30 | 9 | 3.21 | 168.2243 | 8.247945725 | 154.1672098 |
| 25 | 9 | 3.77 | 143.2361 | 8.247945725 | 131.2670407 |
| 20 | 9 | 4.82 | 112.0332 | 8.247945725 | 102.6715235 |
| 15 | 9 | 6.37 | 84.77237 | 8.247945725 | 77.68865675 |
| 10 | 10 | 10.75 | 55.81395 | 9.164384138 | 51.150051 |
| 5 | 1 | 2.21 | 27.14932 | 0.916438414 | 24.88068092 |
| 2 | 1 | 5.29 | 11.34216 | 0.916438414 | 10.39438655 |
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| **Hydrogen MFC** | **Channel** | **2** |  |  |  |
|  | **Usertag** | **H2** |  |  |  |
|  | **Serial Number** | **SMN11211984C** |  |  |
|  |  |  |  |  |  |
| **Valve opening [%]** | **Volume [mL]** | **Time [s]** | **[mL/min]** | **(Corrected volume)** | **Corrected [mL/min]** |
| 40 | 9 | 2.53 | 213.4387352 | 8.247945725 | 195.6034559 |
| 35 | 9 | 2.9 | 186.2068966 | 8.247945725 | 170.6471529 |
| 30 | 9 | 3.36 | 160.7142857 | 8.247945725 | 147.2847451 |
| 25 | 9 | 3.94 | 137.0558376 | 8.247945725 | 125.6032344 |
| 20 | 10 | 5.6 | 107.1428571 | 9.164384138 | 98.18983005 |
| 15 | 9 | 6.34 | 85.17350158 | 8.247945725 | 78.05626869 |
| 10 | 9 | 10.17 | 53.09734513 | 8.247945725 | 48.66044675 |
| 5 | 1 | 2.165 | 27.71362587 | 0.916438414 | 25.39783133 |
| 2 | 1 | 4.83 | 12.42236025 | 0.916438414 | 11.38432812 |
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| **Nitrogen Flush MFC** | **Channel** | **5** |  |  |  |
|  | **Usertag** | **N2FLUSH** |  |  |  |
|  | **Serial Number** | **SMN11211984A** |  |  |  |
|  |  |  |  |  |  |
| **Valve opening [%]** | **Volume [mL]** | **Time [s]** | **[mL/min]** | **(Corrected volume)** | **Corrected [mL/min]** |
| 40 | 9 | 2.28 | 236.8421 | 8.247945725 | 217.0512033 |
| 35 | 9 | 2.63 | 205.3232 | 8.247945725 | 188.1660622 |
| 30 | 9 | 3.04 | 177.6316 | 8.247945725 | 162.7884025 |
| 25 | 9 | 3.62 | 149.1713 | 8.247945725 | 136.7062827 |
| 20 | 9 | 4.64 | 116.3793 | 8.247945725 | 106.6544706 |
| 15 | 9 | 6.06 | 89.10891 | 8.247945725 | 81.66282896 |
| 10 | 9 | 9.32 | 57.93991 | 8.247945725 | 53.09836303 |
| 5 | 1 | 1.96 | 30.61224 | 0.916438414 | 28.05423716 |
| 2 | 1 | 4.43 | 13.54402 | 0.916438414 | 12.41225843 |
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| **Oxygen MFC** | **Channel** | **1** |  |  |  |
|  | **Usertag** | **O2** |  |  |  |
|  | **Serial Number** | **SMN11211984D** |  |  |
|  |  |  |  |  |  |
| **Valve opening [%]** | **Volume [mL]** | **Time [s]** | **[mL/min]** | **(Corrected volume)** | **Corrected [mL/min]** |
| 40 | 9 | 2.24 | 241.0714286 | 8.247945725 | 220.9271176 |
| 35 | 9 | 2.6 | 207.6923077 | 8.247945725 | 190.337209 |
| 30 | 9 | 3.12 | 173.0769231 | 8.247945725 | 158.6143409 |
| 25 | 9 | 3.72 | 145.1612903 | 8.247945725 | 133.0313827 |
| 20 | 9 | 4.65 | 116.1290323 | 8.247945725 | 106.4251061 |
| 15 | 9 | 6.34 | 85.17350158 | 8.247945725 | 78.05626869 |
| 10 | 9 | 9.34 | 57.81584582 | 8.247945725 | 52.98466204 |
| 5 | 1 | 2.04 | 29.41176471 | 0.916438414 | 26.954071 |
| 2 | 1 | 4.84 | 12.39669421 | 0.916438414 | 11.36080678 |
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| **H2S MFC** | **Channel** | **3** |  |  |  |
|  | **Usertag** | **H2SMIX** |  |  |  |
|  | **Serial Number** | **SMN11211984H** |  |  |  |
|  |  |  |  |  |  |
| **Valve opening [%]** | **Volume [mL]** | **Time [s]** | **[mL/min]** | **(Corrected volume)** | **Corrected [mL/min]** |
| 25 | 9 | 3.04 | 177.6316 | 8.247945725 | 162.7884025 |
| 20 | 9 | 3.79 | 142.4802 | 8.247945725 | 130.5743386 |
| 15 | 9 | 5.1 | 105.8824 | 8.247945725 | 97.03465558 |
| 10 | 9 | 7.66 | 70.49608 | 8.247945725 | 64.60531899 |
| 5 | 9 | 15.21 | 35.50296 | 8.247945725 | 32.53627505 |
| 2 | 9 | 36.79 | 14.6779 | 8.247945725 | 13.45139286 |
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