TAMPERE UNIVERSITY OF TECHNOLOGY

ccsp
Carbon Capture and Storage Program

THERMO-CATALYTIC DECOMPOSITION OF METHANE – CARBON PRODUCT UTILIZATION AND MARKET ANALYSIS

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ABBREVIATIONS AND NOTATION

Symbol	Units	Definition
T	K	temperature
T	°C	temperature
p	MPa	pressure (mega Pascals)
p	Pa	pressure (Pascals)
R_u	J/mol K	universal gas constant
M	g/mol	molecular mass
v/v_{ref}	m^3/m^3	volume (m^3) of stored gas in STP conditions in a reference volume of 1 m^3

Abbreviations	
ATP	Autothermal pyrolysis
CCS	Carbon capture and storage
TDM	Thermo-catalytic decomposition of methane
CB	Carbon black
AC	Activated carbon
CNT	Carbon nanotube
MWCNT	Multi walled carbon nanotube
CAGR	Compounded annual growth rate
STP	Standard temperature and pressure (T=0 °C=273.15 K; p=101 325 Pa)

1 INTRODUCTION

Earlier, our research has focused on thermo-catalytic decomposition of methane as route to mitigate CO_2-emissions in natural gas combustion. It has proven to be a working concept. As the decomposition reaction is endothermic, i.e. the reaction taking place consumes energy, different energy input methods are considered. One alternative is to introduce a small amount of oxygen to the reactor. This promotes the partial combustion of the feedstock methane, to support the required reaction enthalpy. The process in then called autothermal pyrolysis of methane.

Thermo-catalytic decomposition and autothermal pyrolysis of methane yield carbon as one of their end products. The aim of this study was to investigate (using literary sources) the possible product carbon morphologies and markets for the produced carbon. Different process catalyst possibilities and their effect on product carbon morphologies are also briefly reviewed. The market study section gives an overview of the most common carbon products and their markets in the World. Finally, some suggestions for pilot plant product carbon utilization possibilities are presented. The focus on this report was on markets and carbon products with large scale possibilities.

2 INTRODUCTION TO CARBON

Carbon has many forms in nature and technology has increased the range even further. Carbon forms can roughly be divided into amorphous and crystalline carbon. In chemistry, amorphous carbon is free, reactive carbon that does not have any crystalline structure, although some short-range order can be observed. Amorphous carbon can be stabilized with hydrogen. In mineralogy, amorphous carbon is the name usually used for coal, soot, and other impure forms of carbon that are neither graphite nor diamond. These forms of carbon, however, are not truly amorphous, but rather polycrystalline structures of graphite and diamond within an amorphous carbon matrix. In Figure 1 the amorphous carbon means the latter, mineralogical, definition. In crystalline carbon (such as diamond and graphite) the carbon atoms are arranged into regular lattices.

Carbon and different carbon derived products have many functions (Figure 1, purple boxes) in different fields, such as chemistry, industry, medical applications, etc. New applications as well as new forms of carbon remain under constant study and development.
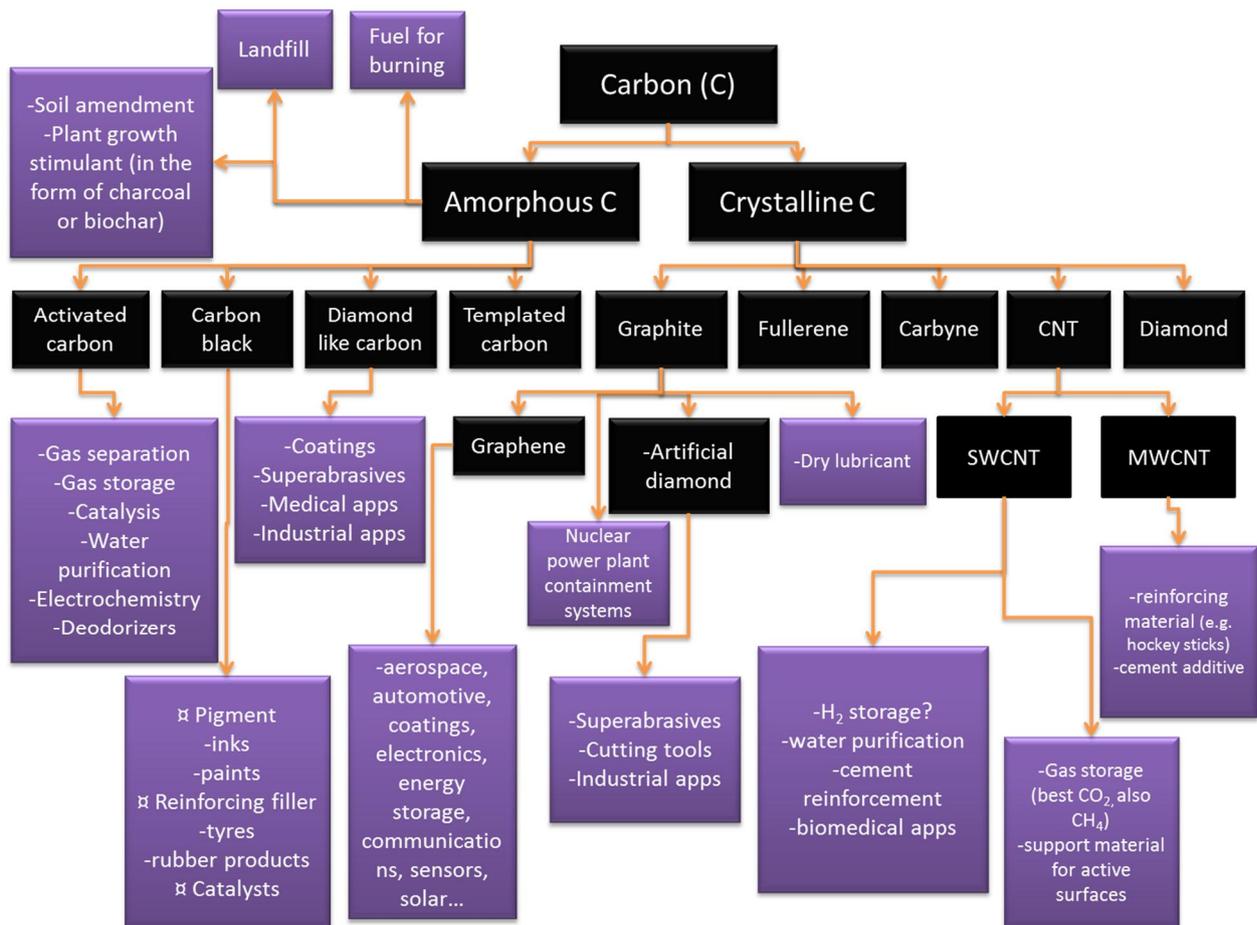
Figure 1 Morphologies of carbon and their possible applications.

3   CARBON PRODUCED BY TDM (ATP)

The production of carbon by autothermal pyrolysis has not been extensively studied. The vast majority of methane degradation studies are for thermo-catalytic degradation of methane (TDM), meaning that no oxygen is involved in the reaction. In fact, thermo-catalytic degradation of natural gas has been employed for decades for the production of carbon black (thermal black process) [1]. The difference between TDM and ATP is that TDM does not produce any CO or CO_2, but only elemental carbon. The produced carbon should not greatly differ between these two processes, although it is not yet clear whether the oxygen present in the ATP reaction is completely converted into gases or whether some of it remains in the carbon product as reactive oxygen surface groups.

ATP and TDM process carbon product morphology depends on the process parameters and catalysts used. Weizhong et al. [2] reported a two stage system using Ni- based catalyst producing both hydrogen and high quality carbon nanotubes. Shah et al. [3] studied several Ni containing catalysts and came to the conclusion that reaction temperature is a key factor affecting the carbon product morphology. At temperatures of about 700-800 °C, the temperature where the catalyst is most active, almost all produced carbon was in the form of multiwalled nanotubes (Figure 2) [3]. At higher temperatures (>900 °C) the carbon deposited is

in the form of amorphous carbon, carbon flakes, and carbon fibers. If no catalyst is used, at temperatures above 900 °C, graphitic carbon film is deposited everywhere in the reactor [3] (preliminary TUT studies). Non-catalytic thermal degradation of methane starts around 1200 °C [4, 5].

Muradov has conducted several studies of methane decomposition [1, 6-9] and found that non-catalytic degradation results in graphitic carbon film and graphite-like carbon depostits (Figure 2). Carbon-based catalysts have been reported to produce graphite-like and amorphous carbon products, as well as carbon black [4, 10-13]. CNT catalyst reportedly induced CNT wall growth [10]. Ni-based catalytst produce carbon nanotubes and nanofibers (500-800 °C), amorphous carbon, carbon flakes and fibers (above 900 °C) [3, 14-18]. Fe-based catalysts require higher temperatures than Ni-based catalysts (around 700-900 °C) to produce MWCNTs and nanofibers [3, 19]. Co-based catalysts produce filamentous carbon and nanofibers in a temperature range from 500 to 900 °C (Figure 2) [20, 21]. Synthetic diamond powder, glassy carbon and graphite have also been tested as catalyst for methande degradation, but they exhibited only low catalytic activity [1]. Note: Guil-Lopez et al. [10] reported different carbon products using different catalysts at 1100 °C (Figure 2, top 3 boxes). It is most likely that at least some of the products already formed during the temperature increase, and not only when the final operation temperature of 1100 °C was reached.
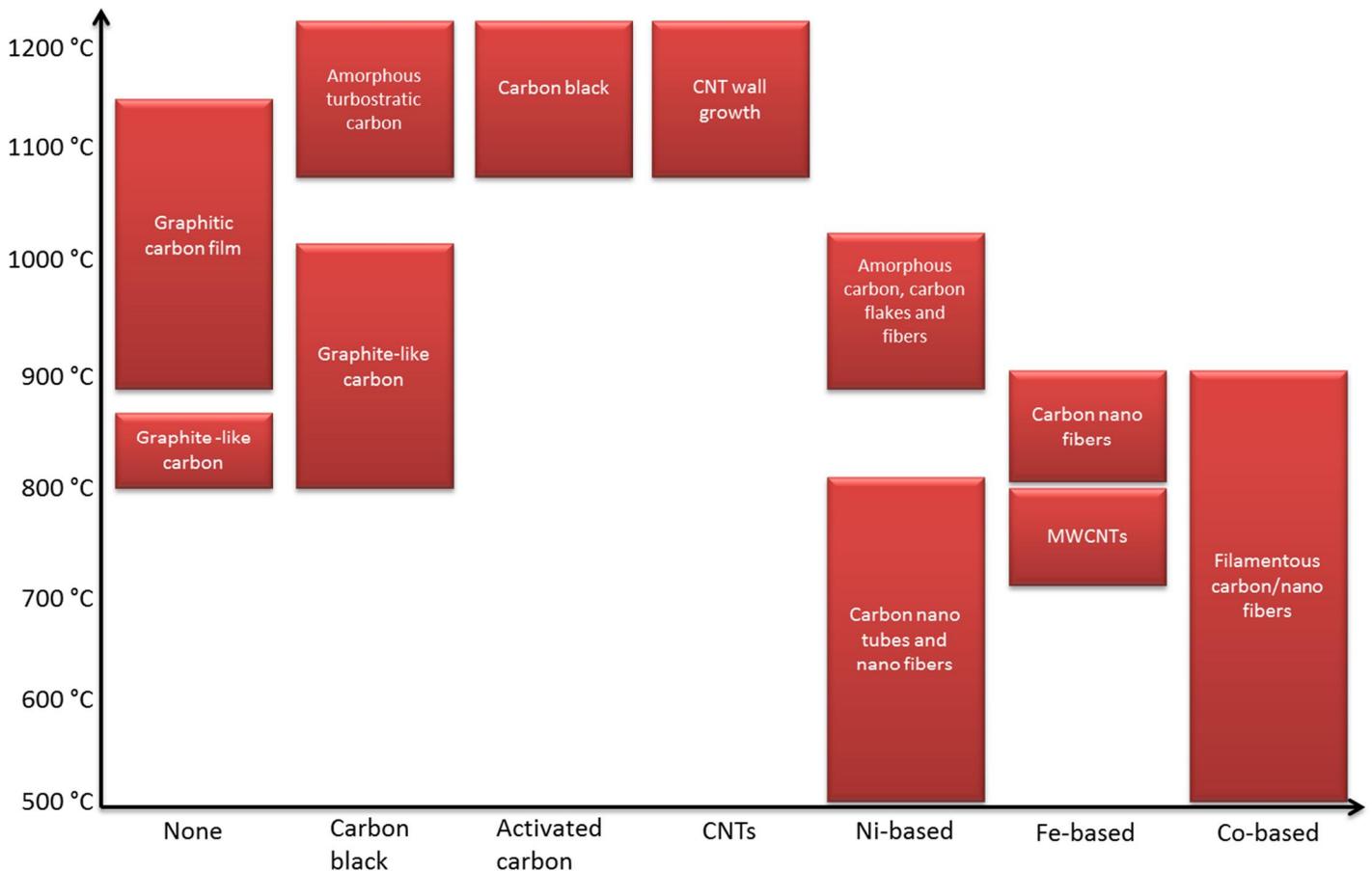
Figure 2 Graphical presentation of literature data on catalysts, temperatures, and carbon morphologies produced by catalytic methane degradation.

- In addition to catalyst composition, reaction temperature is one of the key factors affecting the product carbon morphology.
- Ni-based catalysts have been used most often in catalytic degradation of methane.

4   CATALYSIS AND CATALYST DEACTIVATION

Several different catalysts have been reported in thermo-catalytic degradation studies. The most promising catalysts have been transition metal (Ni, Fe, and Co) based [3, 16, 18-21]. The best catalysts have been combinations of different metals, such as Ni-Cu [16, 18], or metals bound to support materials, such as SiO_2 or Al_2O_3 [22]. Cobalt is, however, used not very often due to higher price and toxicity.

The aim of the catalyst use is to lower the activation energy of the reaction, meaning that the catalytic degradation of methane occurs at lower temperatures than without the catalyst, even up to 500 °C lower reaction temperatures depending on the catalyst [3]. Carbon black catalysts have shown steadier long term catalytic activity compared to the activated carbon catalysts, which often tend to have higher initial activity [23]. Some of the carbon catalysts studied showed only low catalytic activity (graphite, glassy carbon and synthetic diamond powder catalysts). The choice of the catalyst is important because it affects the form of carbon produced in the reaction, and therefore also the possible end uses of the carbon product. The quality of the product carbon can be affected to some extent by the reactor design and reaction conditions as well as by the nature and morphology of the catalyst material. The scientific studies have mainly focused on hydrogen production as well as carbon product and catalyst characterization, so the catalyst material consumption in the reaction is usually not stated.

In the literature reporting the use of metal catalysts, the catalyst is often regenerated by burning the deposited carbon. Some studies mention that it is not feasible to physically separate the catalyst from the product carbon [14]. Therefore, the price of the catalyst of choice can be calculated approximately based on the amount of carbon produced per amount of catalyst metal (Table 1) and the prices of the elements, with some additional costs coming from catalyst preparation and pretreatment methods. The price of Ni was 14 660 USD/t and the price of Cu 7 228 USD/t on 16.8.2013 [24]. The carbon nanostructures produced by using metal catalysts will have at least some contaminants from the catalyst metal [14, 18]. The effect of ATP process oxygen on catalysts and their activity is something to consider in further studies.

According to Ermakova et al. [22] the Ni-based catalysts are active at lower temperatures and provide higher yield of the carbon product per mass unit of the active component. Their study also reported a carbon deposition rate of about 10g/g Ni per hour and carbon yield was the highest with when Ni concentration in the catalyst was 90-96 %. The maximal carbon yield was

also increased by using a textural promoter in the catalyst, and the highest carbon yield (384 g) was obtained using SiO_2 as a promoter [22]. The carbon yield was also observed to depend on the Ni particle size, reaching a maximum at the average particle diameter of 10-20 nm [22]. Takenaka et al. (2003) [17] reported the highest carbon yields using Ni particle size 60-100 nm, whereas Ermakova et al. (1999) [22] achieved the highest carbon production values with metal particles of 10-40 nm average diameter. Reshetenko et al. (2003) [25] achieved the highest carbon yield reported so far (700 g C/g Ni) using $75Ni-15Cu-Al_2O_3$ catalyst with particle size of around 25 nm.

According to Popov et al. [16] the catalyst lifetime increases markedly when the system pressure and catalyst copper content are increased. Higher methane conversion is observed at higher temperatures, but above 600 °C pure Ni catalyst undergo rapid deactivation [16]. The catalyst can be stabilized with Cu doping and the longer service life of the catalyst, as well as increase in the amount of carbon material produced can be achieved by raising the pressure [16].

Table 1 Summary of reaction conditions, catalysts, and the amount of carbon produced per catalyst.

T (K) methane degradation	P (MPa)	PCH4 (MPa)	C produced (g/g Ni)	Catalyst	Reference
948	0.5		244	$82Ni-8Cu/Al_2O_3$	[16]
823		0.1	161	90Ni	[18]
823		0.1	276	87Ni-3Cu	[18]
898		0.1	700	$75Ni-15Cu-Al_2O_3$	[25]
948		0.1	562	$53Ni-27Cu-20Al_2O_3$	[25]
823		-	300	$96Ni-4SiO_2$	[22]
823		-	384	$90Ni-10SiO_2$	[22]
773		0.1	491	$40Ni-SiO_2$	[17]

The catalyst deactivation process depends on the catalyst content. Avdeeva et al. [18] showed that the shape of the metal particles (as well as the carbon morphology) changed dramatically at 9 % Cu addition. The catalyst granules swell due to accumulation of carbon. It is suggested that the Ni catalyst deactivation is due to fragmentation of the metal particles into smaller, inactive units [18]. In the case of the Ni-Cu catalysts it was found that about half of the Ni was atomically dispersed over the carbon filaments due to some kind of erosion process [18]. It was speculated that the inactivation of the catalyst was due to enrichment of the surface Cu content accelerating the deactivation. The rate of atomic fragmentation appeared to be lower than fragmentation by splitting resulting in longer lifetimes of Ni-Cu catalysts compared to Ni catalysts [18]. According to Shah et al. [3] the catalyst deactivation occurred due to encapsulation of the catalyst by graphitic layers and being carried away from the support by nanotubes, meaning that the catalyst is not exactly deactivated, but isolated from the process.

- Best catalysts have been combinations of different metals (such as Ni-Cu)
- Support materials (such as SiO_2 or Al_2O_3) enhance catalytic activity
- Optimal catalyst particle size has varied in different studies from 10 to 100 nm
  - Highest carbon production reported so far was achieved using 75Ni-15Cu-Al_2O_3 catalyst with particle size of around 25 nm

5   PROCESS USE OF PRODUCT CARBON

Process use of the product carbon would be a good alternative because vast quantities of carbon could be consumed in large scale. The carbon produced by ATP could be used as fuel for replacing coal. This would be a large scale option for process carbon utilization but CO_2 emissions would still arise from the burning. It is possible to form carbon slurry that could be similar to fuel oil. It could be used as a replacement fuel in spare and peak load boilers. Since the carbon produced from methane and/or natural gas is pure and doesn't contain ash (therefore there would be no corrosion problems), it could possibly be used in metal industry, for example in the production of iron and steel. The carbon as such will need some treatment, since it is most likely too fine particles to be used in a blast furnace. Agglomeration can be done by sintering or pelletizing the carbon. Gaudernack & Lynum (1998) [26] visioned product carbon (carbon black) use as a reduction material for SiC production (Si, FeSi) and as a carbon additive/carburizer in the steel and foundry industry.

In Germany, BASF, the Linde Group and ThyssenKrupp together with scientific partners VDEh-Betriebsforschungsinstitut, Düsseldorf, and TU Dortmund University, plan to start producing syngas in a two stage process [27]. In the first step, an innovative high-temperature technology will process natural gas to obtain hydrogen and carbon. Natural gas decomposition is achieved thermally, without any addition of oxygen or water. The elemental carbon produced in the process may potentially be used to replace hard coal in the coke and steel industries. The hydrogen is then reacted with large volumes of CO_2, also from other industrial processes, to give syngas. ThyssenKrupp Steel Europe and its subsidiary Kokereibetriebsgesellschaft Schwelgern (KBS) will perform the carbon conditioning and testing for steel industry use. The German Federal Ministry of Education and Research (BMBF) is subsidizing the project within its "Technologies for Sustainability and Climate Protection – Chemical Processes and Use of CO_2" scheme by granting 9.2 million € for the project. The project started on July 1st 2013, and is expected to last three years.

6   CARBON BLACK

Carbon black can be produced through various methods. It is also widely recognized as furnace black, lamp black, acetylene black, channel black, and thermal black. Carbon black is composed of pure elemental carbon and minute contaminants from the manufacturing process. It is

available as powder, pellets, and granules [28]. Carbon black (CB) is a material produced by the incomplete combustion of liquid, aromatic hydrocarbons usually by the oil furnace process [29]. This grade is also called furnace black to distinguish it from carbon blacks produced by other processes. Other production processes include channel process, acetylene black process, and labpblack process [30].

Carbon black is a form of paracrystalline* carbon that has a high surface-area-to-volume ratio, although not as high as activated carbon. In the oil furnace process, CB is produced in a refractory lined reactor, where a flame is produced from air and natural gas. The CB feedstock is atomized into the flame and the CB formation reaction takes place. Downstream from the reaction zone, water is sprayed into the reactor to stop the CB formation reaction. Different grades of CB are produced by altering the reactor geometry, the air flow, gas and feedstock or the position of the water quench.[29]

The main properties of carbon black are structure, particle size and surface chemistry (Figure 3) [30]. In the CB formation reaction the carbon radicals recombine to spherical particles. Depending on the grade produced, the average particle size ranges from about 12 nm to 75 nm [29]. The diameter of primary particles determines the relative color strength (the smaller the particle the higher the blackness) and dispersibility. The primary particles form larger clusters and this property is called a structure [30]. The structure also affects the dispersibility and blackness [29, 30]. Carbon blacks contain small quantities of chemisorbed oxygen on their surfaces. Together with the active carbon sites the surface groups determine the surface chemistry. The affinity of CB with inks or paints, as well as viscosity, changes depending on the type and amount of functional groups. Some grades of CB are given an additional treatment in an oxidative process to increase the amount of oxygen groups on their surfaces [29, 30]. Carbon black can be the product of TDM/ATP and it can also be used as a catalyst for the process.
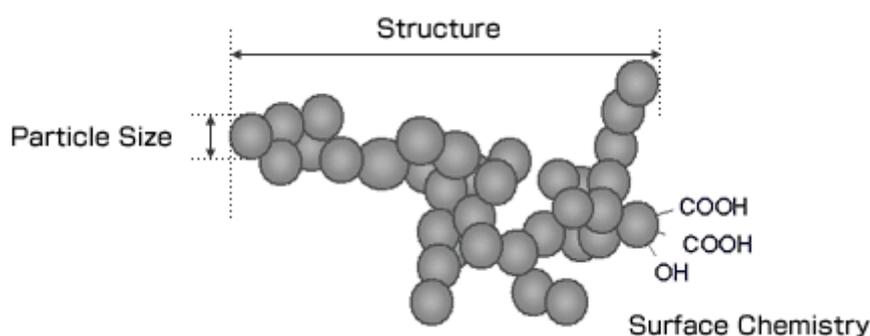
Figure 3 The structural properties of carbon black. Image from Mitsubishi chemical [30].

*paracrystalline: having short and medium range ordering in the lattice (Wikipedia)

7   ACTIVATED CARBON

Activated carbon is an amorphous form of carbon with high porosity. In general, microporosity in carbons is created by removal of the carbon atoms by an activation process. Activated

carbon is commercially available in many forms; powders, pellets, granules etc. The textural properties of activated carbons can be regulated by the preparation conditions and by the choice of carbon precursors.

Activation of carbon can be either chemical or physical. Physical activation methods include steam and carbon dioxide activation, whereas in chemical activation, agents, such as phosphoric acid, zinc chloride, potassium hydroxide, or sodium hydroxide, are used [31]. Chemical activation uses lower temperatures for carbon pyrolysis (the reaction begins at 570 °C using NaOH and at 400 °C when using KOH), most often is done in one step, usually produces higher yield than physical activation, creates very high surface area activated carbons, and microporosity can be well developed and controlled [31]. However, chemical activation is a corrosive process and includes a washing stage [31].

Commercial activation of carbon is usually conducted at temperatures above 800 °C in a mixture of oxidizing agents, steam and cabon dioxide [32]. The largest increases in porosity are produced in the early stages of the activation process, being caused by the opening of constrictions in the porosity and the development of new interconnecting pores [33].

Chemical activation methods mostly produce powdered porous carbons from biomass precursors, which include rubber wood, sawdust, coconut husks, bamboo, rice husks, apricot shell, Jatropa hull etc. [34]. Among the choices available, metal based activating agents, such as KOH, are reportedly more suitable for coal based precursors [34]. Activated carbon is widely used in both industrial and small scale applications. Activated carbon is a strong adsorbent that can be used e.g. in water purification, air filters, medical applications, gas purification, metal extraction etc. Different pore sizes and pore size distributions can be produced during activation to meet the needs of specific applications. Activated carbon can be used as TDM/ATP process catalyst.

One of the ways to characterize and classify activated carbons is their BET surface area. The surface area affects the adsorption potential of the activated carbon, although it is not the only determining factor. Also the pore size and pore size distribution are important properties when choosing an activated carbon. Zhou (2010) [35] expressed that the potential to further improve activated carbon adsorption capabilities is limited because of the difficulty in increasing their already high surface areas, which have already reached 3500 m^2/g. Activated carbon can also be further treated chemically to enhance adsorption of desired products. Table 2 summarizes BET surface areas of some activated carbons used in TDM studies.

Table 2 Summary of BET surface areas of some activated carbons.

Activated carbon	BET surface area m^2/g	Reference
AX21 (Anderson Carbon Co)	2513	[36]
Maxsorb	3178	[36]
KUA6 (KOH activated Spanish anthracite)	3808	[36]
A-MWNT (chemically activated nanotubes)	1220	[36]
Slitpore (computer model, for comparison)	2620	[37]

Pore size range definitions:
- micropore < 2 nm
- mesopore 2-50 nm
- macropore >50 nm

Different size pores and different size grains are needed for different applications.

8 GRAPHENE

Graphene is formed from a single layer of carbon, sourced from raw graphite [38]. The ultimate production costs are, therefore, dependent on the price of graphite. Graphene is the world's strongest, thinnest and most conductive material, while also being transparent and flexible [38]. It is predicted to be the next big thing after carbon nanotubes.

There are different technical ways to manufacture graphene. Different methods yield different types of graphene, differing in their microstructure, layer number, oxygen content, etc. Each type offers a different set of properties targeting different set of markets [39]. Most graphene producers currently produce graphene nanoplatelets and graphene oxide [40]. Vaporized product carbon might be suitable for graphene production through chemical vapor deposition, although elemental carbon vaporization requires extremely high temperature, and therefore, consumes a lot of energy.

According to Jari Kinaret's (coordinator of graphene flagship project) presentation given at Future Science and Technology –day at TUT on 25th Sept 2013, graphene is an impermeable material, even to He atoms. Graphene also adsorbs light at any wavelength. The advantage of graphene over nanotubes is that it is compatible with planar technologies due to the flat structure. Graphene has started an intense research on other 2D materials, such as WS_2, boron nitride, MoS_2, and their combinations.

9 ATP/TDM PRODUCT CARBON

There are many possible uses for the ATP/TDM product carbon depending on the purity and quality. Using 2005 figures, it was estimated that if 50 % of natural gas (NG) available in USA would be converted to hydrogen and carbon via catalytic decomposition, close to 40E6 tons of carbon would be produced [15]. World carbon black consumption now is 9,4E6 tons per year [41]. Clearly, all carbon markets combined would not be able to absorb such quantities. Actual research for carbon end product utilization is scarce, although the possibilities of product end-use are often speculated.

9.1 Construction industry and energy generation

Potential large carbon markets would be building and construction material development, such as cement industry [6, 15, 42]. Composite production would be also interesting to aerospace and automotive industries [15]. The production parameters and, for example, catalysts have to be optimized for suitable carbon output. The use of the carbon product for electricity production [15] by direct carbon fuel cells is also dependent on the ATP vs TDM choice and the quality of the produced carbon.

9.2 Environmental use and carbon storage

Other large carbon product sink could be amelioration of soil [15]. It has been demonstrated that adding carbonaceous products (e.g. charcoal) to soil can significantly increase seed germination, plant growth, and crop yields [43]. The reasons for improved crop yields include better water retention, and maintaining high levels of soil organic matter and available nutrients [43]. This market could practically be unlimited [15]. However, spreading carbon dust on fields is probably not the best solution, therefore the carbon would have to be treated (e.g. pelletized) to minimize possible health risks. This would add another step and costs to the process.

Not all carbon products are suitable for soil amelioration. For example graphene and nanotubes can have detrimental effects on flora and fauna [44, 45]. Carbon products for environmental applications would most likely have to be amorphous carbon with relatively high surface area. In Australia, biochar has been studied in soil amelioration purposes [46]. The greatest positive effects of biochar have been in highly degraded, acidic, or nutrient-depleted soils [46]. The use of ATP/TDM product carbon on soil and plants would have to be further evaluated.

It is possible that due to the enhanced nutrient holding capacity of the carbon-amended soil, the amount of fertilizers could be substantially reduced, resulting in a further economic gain (the majority of fertilizers cost 115-215 US dollars per ton in 2005) [15]. Increased charcoal addition to soil may, however, reduce crop yields, and the optimum range might have to be determined individually for each type of plant and soil [43].

As an inert material under ambient conditions the product carbon could be stored for extended period of time making soil amelioration a possible carbon capture and storage technique [6, 43]. For an estimate of the CCS market size, the IEA expectation is for 100 projects required globally by 2020 at 2 billion US dollars each, meaning a global market of 200 billion US dollars (cumulative) in the next 8 years [47].

9.3 Gas adsorption storage

Product carbon could be activated and used for natural gas adsorption storage. Adsorption storage requires lower pressures than compressed natural gas storage systems, and can be operated at ambient temperatures. Adsorption storage could be an option for mitigating peak

load demand. Use of activated carbon as an adsorbent material for gas storage has attracted a lot of attention, and also shown some promise.

The main factors affecting adsorption capacities of CO_2 and CH_4 on activated carbons is the textural properties of the carbons [48]. The properties can be modified by preparation conditions and carbon precursors. The major problem with adsorption gas storage is the selectively stronger adsorption of higher molecular weight hydrocarbons and sulfur-based odorants [49]. During charge these compounds adsorb preferentially over CH_4 and tend to remain in storage at exhaust pressure. This in time leads to blocking of micro pores and adsorption capacity loss [49].

The problems arising e.g. from natural gas composition can be circumvented by technical design of the storage. When storing natural gas the gas is upon filling passed through a small carbon bed, which adsorbs the higher molecular weight hydrocarbons before the gas enters the storage vessel [50]. With this system the blocking of the storage carbon is avoided. When the gas is discharged, the smaller carbon bed can be heated to aid desorption of the heavier hydrocarbons back into the gas stream [50].

Carbon dioxide adsorption has attracted attention because it could be used as a potential carbon capture and storage technique. One possible carbon capture and sequestering approach is adsorption of CO_2 either before or after burning carbon containing fuel. The success of CO_2 adsorption largely relies on the development of a low cost adsorbent with a high CO_2 selectivity and adsorption capacity [51]. The reported CO_2 preference over CH_4 could possibly be utilized in CH_4 purification from natural gas or biogas [48, 49].

Yang et al. studied adsorption capacities of different gases at 25 °C under pressure range 0-200 kPa. The results were that the highest adsorption capacity for CO_2 was 2.55 mmol/g at 200 kPa and for CH_4 1.93 mmol/g at 200 kPa. Matranga et al. [37] did simulation analyses for pure CH_4 adsorption on theoretically optimal carbon structure. They compared the results to compressed natural gas (CNG) and gasoline. The results of Matranga et al. [37] are presented in Table 3.

Table 3 Theoretical values for carbon adsorbed natural gas (methane) [37].

	Adsorbed natural gas at 3,4 MPa		Compressed natural gas at 20,7 MPa	Gasoline
	Monolithic carbon	Pelletized carbon		
Max theoretical storage capacity v/v_{ref}	209	146	240	-
Max theoretical delivered capacity v/v_{ref}	195	137	216	-
Max delivered energy density	0.25	0.17	0,29	1,0

A large part of the research on gas adsorption storage methods is done for vehicular purposes. The U.S. Department of Energy has set the target for material-based adsorbed methane storage at 180 m^3(STP)/m^3 at 298 K and 35 bar (m^3(STP)/m^3: the standard temperature and pressure equivalent volume of gas per volume of the adsorbent material) [35]. Natural gas vehicles have the potential of lowering polluting emissions resulting from traffic [50]. Adsorbed natural gas has been one of the suggested fuel options because it requires lower pressures (only single stage compression required) than compressed natural gas, and it can be stored at ambient temperatures [50]. For vehicle applications, maximum gas storage density is the ultimate requirement, in order to produce vehicles with acceptable mileage range [52].

Bulk storage applications, have different issues to be considered. Bulk storage applications are critically dependent on the cost of the adsorbent material [52]. High-performance, high density carbons, which would be suitable for vehicle use, tend to also have high costs. A compromise in cost/performance is, therefore, required, which leads to a very different choice of carbon for large scale storage applications compared to small scale vehicle applications [52]. According to Judd et al. [52] the carbon used for large scale storage applications is more likely to be in the 80-100 v/v_{ref} range.

Table 4 summarizes different carbon materials and their methane storage and delivery potentials reported in literature. The values in the table have been obtained from several different sources. The storage capacities calculated here for Table 4 are presented in the reference volume of 1 m^3 according to the ideal gas equation in STP conditions.

Table 4 Different carbon materials and their methane storage and delivery potentials reported in literature.

Storage material	Storage temp. K	Storage pressure MPa	Storage v/v_{ref}	Delivery v/v_{ref} (0.1 MPa)	Delivery %	Storage capacity kg/m^3	Ref.
Monolithic C (theoretical simulation)	300	3.4	209	195	93.3	150	[37]
Pelletized C (theoretical simulation)	300	3.4	146	137	93.8	104	[37]
Optimized carbon pores (theoretical simulation)	274	3.4	249	-	-	178	[53]
Zeolite pores for comparison (theoretical simulation)	274	3.4	79.65	-	-	57	[53]
Self-prepared AC	298	4	155	145	93.5	111	[54]
Self-prepared AC fibers	298	4	163	143	87.8	117	[55]
AC fibers prepared from commercial fibers	298	4	166	150	90.4	119	[55]
Commercial carbon material A20	298	4	155	140	90.3	111	[55]
Self-prepared powdered AC	298	4	166	142	85.5	119	[55]
AC fibers	298	4	163	143	87.7	117	[56]
KOH activated C from corn cobs	298	10.3	160	-	-	115	[57]
DOE target (for comparison)	298	3.5	180	-	-	130	[35]
Compressed natural gas (for comparison)	298	20.7	240	216	90.0	172	[37]
Compressed natural gas (for comparison)	298	3.5	33	-	-	23.4	[55]
Liquefied natural gas (for comparison)	113	0.1	600	-	-	400	[55]
Uncompressed natural gas (for comparison)	298	0.1	1	-	-	0.72	

The storage calculations state only the density of the adsorbed gas. The density of the carbon material is not included in the calculations. The packing density of the carbon material varies, but is roughly in the 450-1100 kg/m^3 range [55]. Usually the packing tests are done at small scale. In large scale applications the form of the carbon material (pellets, powder) and also the form of the storage vessel can affect the packing density.

Adsorption storage of hydrogen has also been extensively studied. Hydrogen storage, however, seems not to be feasible on activated carbons at ambient temperatures. Doping of the storage material and graphene storage have shown some promise, but experimental results are still far from the theoretical simulations. Lithoxoos et al. [58] and Oriňáková & Oriňák [59] have studied hydrogen adsorption on carbon nanotubes. Adsorption uptake of different gases on single walled carbon nanotubes was reported to increase in the following order: $H_2 << N_2 \approx CH_4 < CO << CO_2$ [58]. Both investigations came to the conclusion that hydrogen can't be efficiently stored adsorbed on nanotubes either [58, 59]. H_2 storage capacity of CNTs is small at room temperature and significant adsorption is observed only at very low temperature or high pressure [59]. New ways to store hydrogen on nanotubes and metal-organic frameworks (MOFs), ceramics etc. are being investigated. Production of nanotubes by ATP is possible, but requires a metal catalyst and the quality of the product depends on the operation parameters [10, 19].

Optimal pore sizes for gas adsorption:
- methane 1.14 nm
- hydrogen 0.66 nm
- carbon dioxide 0.5-0.7 nm
- pore size distribution is crucial for efficient adsorption
- larger pores play a role in gas transportation in and out of the smaller pores

CH_4 and NG storage capacity analyses of ATP produced carbon and comparisons to other carbon materials can be performed at TUT. Comparisons of pure CH_4 and NG adsorption can be made in a laboratory scale. Nanotube production and product analysis can be conducted in collaboration with surface analysts at TUT.

9.4 Activation of carbon

The product carbon, if in suitable non-crystalline form, can be activated [48, 60]. Due to large multinational companies operating in this field, it is most likely not economically feasible. If the carbon is of good quality, selling the carbon as such might be an option. Activation of the product carbon for ATP process catalyst can be tested at TUT laboratory. Using the product carbon for ATP catalyst would consume only a small portion of the carbon produced. It would eliminate the need to buy catalyst carbon, but also it would mean more costs for the process, since the activation has some requirements. Also, it is good to bear in mind that self-activation in small scale might lead to greater batch to batch variations than commercial products, and therefore, to some process instabilities.

9.5   Landfill and burning

If the carbon produced is a mixture of different forms, it is most likely not feasible to separate and purify them. Then the best options for the product might be landfilling or burning the material. Landfilling large amounts of carbon might be costly. Burning the carbon could provide heat for the process and/or substitute coal in some cases. The ATP product carbon would be NOx, SOx, and ash free and therefore emissions from burning would be CO_2 and possibly soot. As carbon slurry the material could be pumped instead of transported to the burning facilities and used similar to fuel oil.

10 HEALTH CONCERNS

Carbon products are possible health risks. For example, activated carbon dust is irritating to respiratory tract and wet dust reduces oxygen available for breathing [61]. Carbon black is classified as potential human carcinogen and can cause decreased pulmonary function [62]. Carbon nanotubes are bio-persistent and can exist as fiber-like structures. Animal studies have shown adverse lung effects and some reports show asbestos-type pathology [44]. Graphene has been shown to inhibit the growth of some plants, cause necrotic lesions, electrolyte leakage and oxidative stress [45]. Suitable personal protective equipment should be selected and used after consulting available performance data for each type of carbon product. Waste disposal methods should be determined depending on the type of carbon product.

In addition to carbon catalysts, metallic catalysts might have risks to the environment and humans. Material safety data sheets and other safety information provided by the catalyst manufacturer should be consulted. Appropriate procedures, protocols, and protective equipment should be used when working with these materials.

The health impacts of carbon products are not clear and long term data is not available for all materials. Therefore, these issues should be part of the future research plan. Health and environmental impacts should be monitored and updates on the most recent research results should be followed.

CARBON PRODUCT MARKET ANALYSIS

Table 5 Summary of carbon product market size and worth according to literature. Estimations of future prospects according to literature.

C product	production/consumption/ market size/market worth	estimation	Reference
Carbon black	9E6 t/year (2013)	13E6 t/year (2015)	[63]
Carbon black	9.4E6 t/year (2013)	growth 4.3 %/a through 2013	[41]
Carbon black/tires (largest consumer)	7.8E6 t (2011)		[64]
Carbon black		12E6 t/year (2015)	[65]
Activated carbon	300 000 t (2006?)		[66]
Activated carbon		over 10 %/year increase through 2016 to 1.9E6 t	[67]
Activated carbon	China 2012 production 521 100 t	China 2015 production 574 000 t	[68]
Activated carbon	China 2012 consumption 303 000 t	China 2015 consumption 448 000 t	[68]
SWCNTs	36.8E6 $		[69]
Nanotubes	several thousand tons per year		[70]
Nanotubes	production capacity 2010 2 500 t	production capacity 2016 12 800 t	[69]
Nanotubes	668.3E6 $		[69]
Nanotubes (various kinds)	192E6 $ in 2011	CAGR 22.4 % reaching 527E6 $ by 2016	[71]
MWCNTs	219E6 $ in 2012	CAGR 9.1 % to 292E6 $ by 2016	[71]
MWCNTs	631.5E6 $		[69]
Graphene	9E6 $ (2012)	126E6 $ (2020)	[72]
Graphene		122.9E6 $ (2017)	[73]
Graphene		896E6 $ (2022)	[73]
Synthetic diamond monocrystals	In China 88 % of production	Growth in China over 10% annually	[74]

CAGR= compound annual growth rate

11 CARBON BLACK

The primary end-application of carbon black is the rubber market sector, such as the tire industry. Currently, tires and rubber products account for about 90 % of global carbon black market [65]. Non-tire applications include conveyor belts, flaps, hoses, and gaskets. Carbon black has been classified as possible human carcinogen (Group 2B) by International Agency for Research on Cancer (IARC) [28]. Increase in demand of CB in paints, inks, and coatings is predicted for the near future. Demand for non-rubber applications using mainly specialty blacks will increase significantly. Another emerging area is metallurgy [65].

CB manufacturers are major emitters of CO_2 [28]. Silica and other silanes are expected to emerge as major substitutes of CB due to better performance and environmentally friendlier nature. These products reduce rolling resistance in tires and therefore improve fuel efficiency [65].

11.1 World

Worldwide CB consumption is about 9E6 t/year in 2013 [41, 63]. The global CB market is worth 15 billion US dollars [75]. Average global growth will likely exceed 4 % over the next five years [63]. Consumption is expected to reach 12-13E6 t/year in 2015 [63, 65]. Growth in the non-tire rubber product market will outpace growth in the tire sector, while the special blacks market will rise the fastest [41]. Largest CB producers include multinational companies such as Degussa AG, Cabot Corp, and Columbian Chemicals Company which together hold 50-60 % of the total volume [28].

11.2 USA

In 2000 in USA, CB shipments were more than 1 billion US dollars, and CB was sold at 28-46 cents per pound depending on the grade [76]. In 1996 CB sold for 28-50 cents per pound [76]. The USA market size for CB is estimated at about 1.6E6 t (in 2010?) [65].

11.3 China/Asia-Pacific

Asia-pacific is the largest market for carbon black in the World, with a share of 37 % [65]. China is the largest CB producer and exporter in the World and it will consume nearly 35 % of global CB by 2017 [77]. In 2011 the installed capacity in China was over 5E6 ton/annum and the CB market is expected to grow at the compounded annual growth rate (CAGR) of nearly 6 % in 2012-2017 [77].

12 ACTIVATED CARBON

12.1 World

The next four years (2013-2017) could see activated carbon (AC) demand almost double [68, 78]. The increase is largely due the power plant standard, and the cement and industrial boiler mercury control standards coming to effect in April 2015 in the USA, which will increase the demand in North America (Figure 4) [78]. AC prices increased steadily from 2007 to 2012 and the price development for the years 2012 through 2017 is expected to be rising again [78].

Liquid phase end uses account for about 80 % of total AC consumption, while gas-phase uses accounted for 20 % of the world market [68]. Gas-phase use is expected to increase the market share to 2017 [68]. Figure 4 illustrates the market development in the World through 2006-2011 and estimation for 2011-2016. Figure 5 presents the history and estimated development of activated carbon demand in the World.
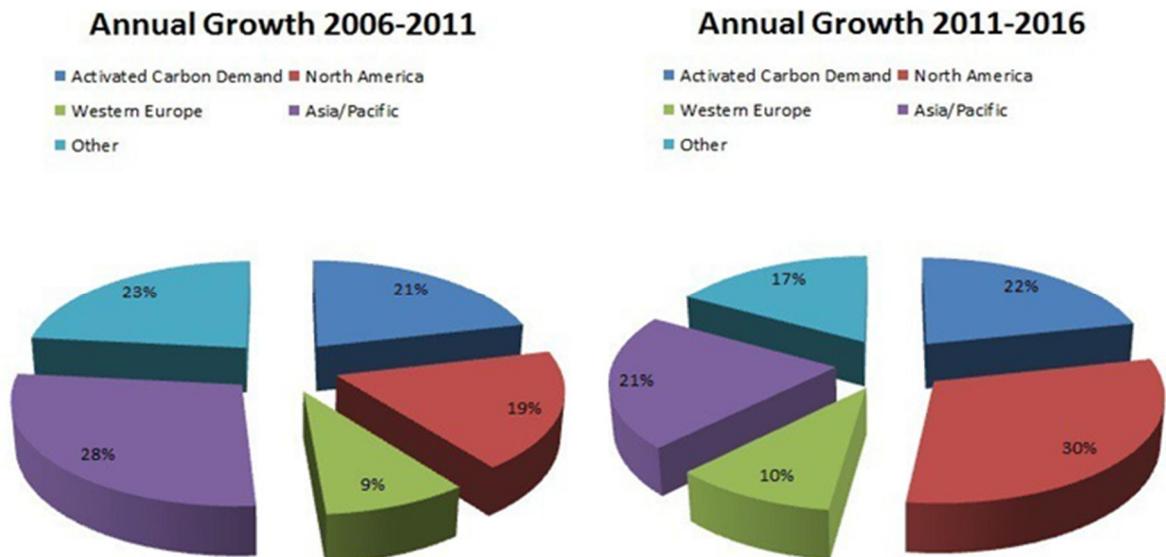
Figure 4 Market development for activated carbon in the World. US legislation changes will increase the demand in North America [79, 80].
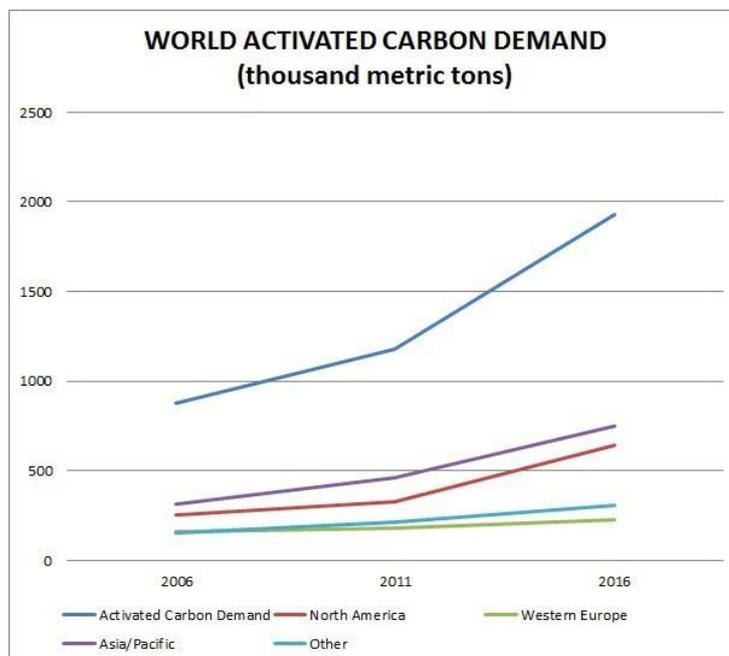
Figure 5 History and estimation of World activated carbon demand [81].

12.2   USA

The new environmental and mercury standards are expected to increase the market for powdered AC by approximately 300 000 t per year before 2017, 11.2 % per year to almost 6E5 t in 2017, with market value reaching 1.8 billion US dollars [78, 82, 83]. The market for powdered AC in mercury control applications grew 101 % per year in 2007-2012, compared with an average overall growth for all applications of 13 % per year [68]. Powdered products will expand their market share to 70 % of total US demand in 2017 [82]. A new waste water treatment rule is expected to increase the US market for granulated AC by at least an

additional 35 000 t per year by 2017 [78]. AC use in food and beverage processing and solvent recovery will remain stable [82].

12.3 China

In 2012 the AC production in China grew to 521 100 t while the domestic demand was 303 000 t [68]. The estimation is that the production and consumption of AC in China will grow steadily till 2015, with the production reaching 754 000 t and domestic demand 448 000 t [68].

13 NANOTUBES

Main end-user markets for nanotubes are composites for sporting goods, conductive additives for lithium-ion batteries, fuel system components, AFM tips and plastic additives [84]. Figure 6 illustrates the shares of global CNT market by industry. While the cost of CNTs was once prohibitive, it has been coming down to about 10 US dollars/m^2 for film applications [85]. Prices of MWCNTs range from 40-70 US dollars/kg, depending on quality, with Chinese manufacturers offering MWCNTs at lower prices [84]. Prices for CNTs are expected to fall by an average of 15 % over the years 2012-2016 as large companies are starting to produce commercial-scale volumes of CNTs and companies in China and Russia will push significantly cheaper CNTs in to the market [69]. In 2011, CNTs accounted for a 28 % market share of overall nanomaterials demand [69].
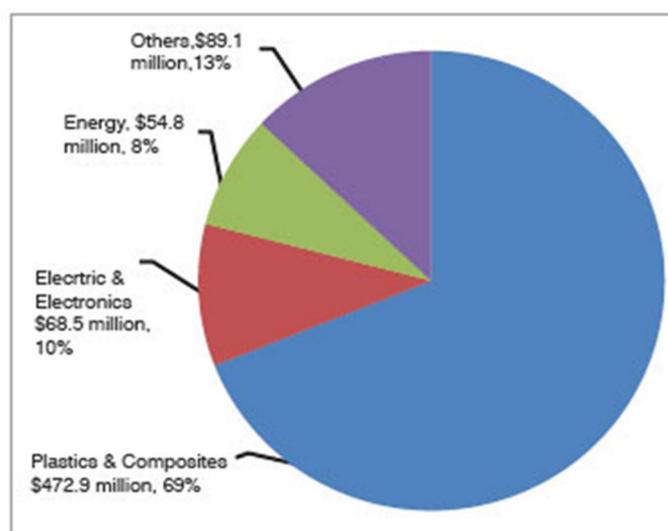
Figure 6 Global CNT market by industry [69].

The global CNT industry turned over around 668.3 million US dollars in 2010, with MWCNT production value of about 631.5 million and SWCNT production value of around 36.8 million US dollars [69]. The production capacity exceeds the actual production and only about 25 % of the global CNT production capacity was in use in 2010 [69, 84]. At the end of 2010 the production capacity for CNTs reached 2 500 tons and is expected to exceed 12 800 tons in

2016 (Figure 7). Asia-Pacific is the production leader, followed by North America and Europe [69].
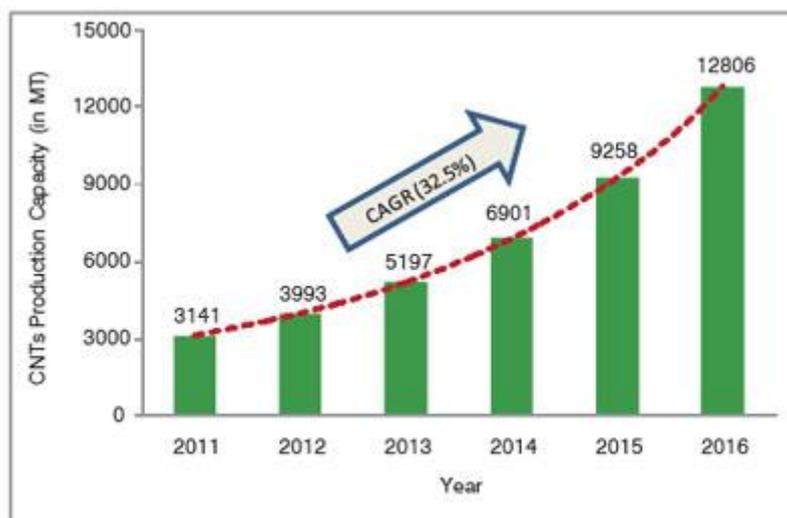
Figure 7 Forecast (2011-2016) for global CNT production capacity [69].

The challenges in the future might be that nanotubes are in danger of being replaced in conductive applications by graphene and in composites by nanocellulose, although CNTs will remain competitive especially in composites and electronics applications [84]. A number of issues, including high costs, inconsistent quality across the supply chain, dispersion and compatibility with matrix material, and toxicology also still need to be addressed [69, 84].

14 GRAPHENE

Large markets interested in graphene products are aerospace, automotive, coatings, electronics, energy storage, communications, sensor, solar, oil, and lubricant sectors [40]. It is predicted that graphene market is set for 40 % annual growth, from 9 million US dollars in 2012 to 126 million US dollars in 2020 [72]. The value of graphene has increased from about 1000 US dollars per ton in 2009 to about 3000 US dollars per ton in 2012 [38]. The largest market will be graphene nanoplatelets, used mainly in composites and energy storage applications [39].

Another forecast is that 100 million US dollars' worth of graphene will be sold in 2018 into a range of applications, including RFID (radio frequency identification), smart packaging, supercapacitors, composites, ITO replacement (indium tin oxide), sensors, etc (Figure 8) [39]. A third forecast shows that the global market for graphene-based products will reach 122.9 million US dollars in 2017 and 986.7 million US dollars in 2022 (Figure 9) [73]. Major challenges like high costs, processing issues, and competing materials are among the issues to be overcome in the near future [72].
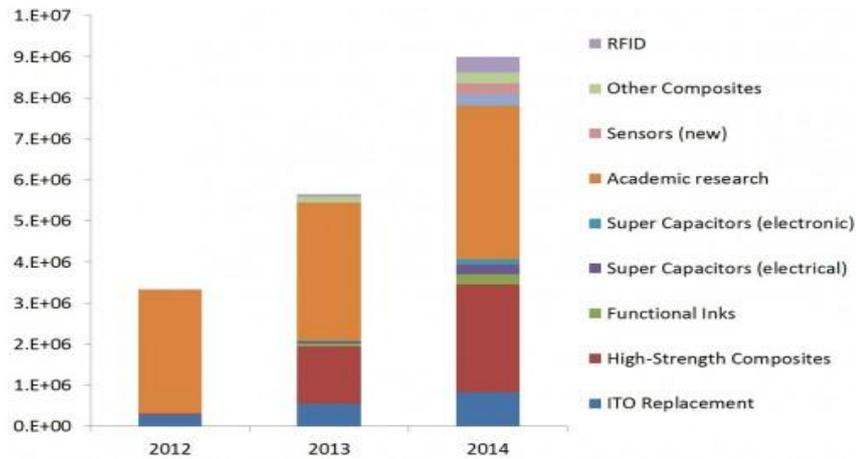
Figure 8 Market value per application sector [39]. (Original figure source IDTechEx.)
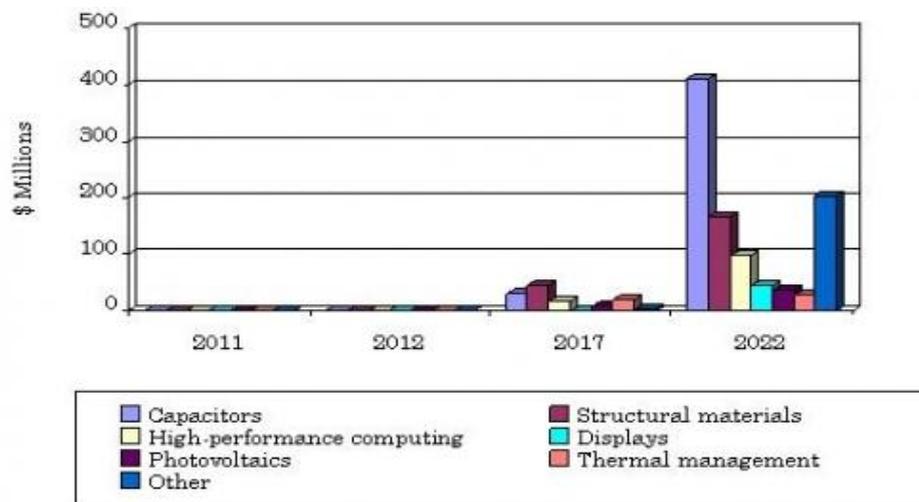
Figure 9 Global market for graphene-based products 2011-2022 (million US dollars) (original source BCC research) [39].

According to Jari Kinaret's presentation, chemically exfoliated graphene nanoplatelets cost about 935 €/100 g, chemical vapor deposition goes for 675 €/10 cm wafer on SiO_2, and mechanically exfoliated graphene (scotch tape method, used for research) is 5 €/μm^2.

15 OTHER USES

Carbon based products are also used in electrochemistry, superabrasives, medical applications, and as a material to create artificial diamonds. The markets for these products are substantially smaller than the markets for the products described above, and therefore, will not be described here in more detail.

16   FURTHER MARKET INFORMATION

An international, commercial market study is available for most of the carbon products. They can be purchased through internet and the price range is about 2000-6000 US dollars for a single license. These market studies cover the history and future prospects as well as global and regional statistics and forecasts.

Examples of market studies available:

Carbon black: http://www.ceresana.com/en/market-studies/chemicals/carbon-black/

Activated carbon: http://www.reportlinker.com/p0937503-summary/Global-Activated-Carbon-Market-Forecast-and-Opportunities.html

Carbon nanotubes: http://www.transparencymarketresearch.com/carbon-nano-tubes-market.html

Graphene: http://www.idtechex.com/research/reports/graphene-opportunities-2013-2018-technology-markets-players-000333.asp

Industrial diamonds:
http://www.researchandmarkets.com/reports/660047/industrial_diamond_market_review

17   POTENTIAL MARKETS IN FINLAND

Markets for carbon products in Finland are very limited compared to the global scale. For a pilot scale ATP/TDM plant it would, however, be very important to find possible applications nearby for the carbon produced in the process. The pilot scale plant study should include investigation on the suitability of different product carbons on various real-life applications. The following is a list of possible applications from which some might need more further research than others. Potential collaboration partners / companies that might be interested in the technology are also listed.

Currently employed technologies or technologies very close to practical applications include:

Industrial uses
- paint pigment (Tikkurila, Coloria Oy, Virtasen maalitehdas, etc.)
- rubber industry (Nokian Tyres, Suomen rengastehdas, Metso minerals Finland, etc.)
- carbon fiber composite structures for steel replacement
- catalysis
- electrochemistry – conductive and insulating materials
- extra hard composite materials for medical applications and superabrasives

Clean tech uses
- toxin removal from soil and water by adsorption
- biogas purification (Gasum, other biogas producers)
- gas separation (e.g. CO_2 removal)
- water purification

Possible future applications needing further research include:

Industrial uses
- iron and steel industry, possible blast furnace fuel or fuel additive
- carbon slurry as a fuel oil replacement (Wärtsilä, Neste Oil)
- new fuel products or fuel additives (vehicle or energy production fuels) (Neste Oil)
- cement additives (Nordkalk)
- natural gas or methane adsorption storage (Gasum, other biogas producers)
- graphene production

Clean tech uses
- soil amendment (water retention and soil texture improvement)
- nutrient adsorption and use as simultaneous soil amendment material and fertilizer (Kemira, biogas producers)
- odor control in agriculture (manure processing on-site so that the process heat can be used in e.g. animal shelters without massive odor nuisances)
- concentration of gases and interesting compounds and their controlled release for further treatment or applications (e.g. ammonia, CO_2 and phosphorus compounds)
- large scale water purification (Talvivaara, Kemira, waste water treatment plants)
- air and water protection applications (power plants, farmers etc.)
- removal of pharmaceutical and personal care residues from water (waste water treatment plants, Kemira)

18   SUMMARY

Carbon comes in many forms and is used in multitude of applications. Carbon forms can roughly be divided into amorphous (non-ordered crystal lattice) and crystalline (ordered crystal structure) carbon. The newest members of carbon family are nanotubes and graphene, both of which are under continuous research and development.

Different carbon products can be formed during TDM/ATP processes. Reaction conditions and catalyst composition highly affect the morphology of the product carbon. Optimization of the process needs to be done according to the end product needs. For example, higher quality nanotubes might result in lower methane conversion rate etc.

Changing the carbon from one form to another might be technically possible in some cases (e.g. activation or surface group modifications, or transforming graphite into diamond) but it will add costs to the process. The most economical alternative would be to find applications for the product carbon with minimal downstream processing, or to find a way to produce very high value end products with more complicated process.

Health impacts are not yet clear for all carbon products, but hazards must be borne in mind and sufficient safety measures have to be followed.

There are possibly large markets for produced carbon. Some of the markets are just emerging, some have already peaked, and some need still further scientific studies. Domestic markets have also potential for product carbon use. Networks with possible carbon users should be created and their needs for products should be discussed.

Large scale possibilities for product carbon use might be for example:
- fuel use as carbon slurry or fuel additive
- soil amendment or soil storage of carbon
- construction industry; cement additive
- activated carbon production for storage and purification applications
- tire, paint, and rubber industry, if good quality carbon black is produced

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