Techno-Economic Assessment of Carbon Utilisation Potential in Europe

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The purpose of this work is to analyse different carbon capture and utilisation (CCU) options, and hence to identify the role of CCU on the future European energy and industrial sectors. This work carries out the techno-economic analyses of methanol synthesis and accelerated aqueous carbonation of waste (fly ash) as two differentiated options for CO_2 conversion. Process flow modelling is used to evaluate the operational and cost performances of two conceptual designs. Calibration and validation of the models are completed to then assess diverse operational, economic and environmental key performance indicators (KPIs). The inlet CO_2 and fly ash originate from a conventional power plant. The needed hydrogen for the methanol case is produced by water electrolysis. The work puts into relevance the differences in performance and costs for the two processes analysed. Future work will contemplate other CCU processes and a global market study in the European context that focuses on (i) current prices and demands for the products, and (ii) the analysis of their foreseen market evolution and price elasticity.

1. Introduction

The contribution of fossil fuels to the energy share is foreseen to be more important than renewables and nuclear power at short and medium term. Moreover, process industries like cement, iron and steel, aluminium, paper and pulp and refineries, have inherent CO_2 emissions as a result of raw material conversion. In this context, carbon capture utilisation and storage (CCUS) is presented, at least, as medium term alternative to mitigate climate change. CCU represents a new economy for CO_2, as it is used as raw material for other processes. This includes the synthesis of chemicals (such as methanol or formic acid), production of inorganic substances (like calcite, after the mineralization of CO_2) and applications based on CO_2 physico-chemical properties (for example when used in the food and beverage industry) (Peters et al., 2011). CO_2 utilisation delays carbon emissions to the atmosphere while reducing the consumption of the original feedstock and avoiding the emission of other substances associated to them. Enhanced oil and gas recovery (EOR, EGR), as well as CO_2 mineralization, result in permanent storage, while in the other utilisation cases, CO_2 is emitted later in the product chain, i.e. when the CO_2-product based is consumed. CCU, due to its inherent potential, is considered a complementary alternative to geological CO_2 storage: the predicted short-term market potential by Aresta et al. (2013) is around 300 $MtCO_2$/y, compared to about 14,000 $MtCO_2$/y emitted from large point sources (Boot-Handford et al., 2014). The market for CO_2 utilisation is relatively small, and future markets for CO_2 will have to map and prioritize points of CO_2 emission with utilisation opportunities, advocating for tailor-made and local solutions (GCCSI and PB, 2011). The different utilisation alternatives and carbon capture and storage (CCS), will have to work in optimum portfolios of options, i.e. different technology mix regarding the specific CO_2 emitters, transportation and storage/use solutions of each local area analysed.

This work analyses two carbon utilisation options: methanol synthesis and mineralization of CO_2, with two well differentiated potentials. Methanol (CH_3OH) is typically produced by the Fischer-Tropsch process, the catalytic conversion of syngas usually coming from steam reforming of CH_4. Its current market is around 40 Mt (produced in 2007). Future market will be larger if considering its potential as blended with gasoline, or converted into gasoline or diesel substitutive (dimethylether). The produced mineral considered here is

calcite ($CaCO_3$), that can be disposed, used in mine reclamation, in the building industry, as a polymer filling material, as pharmaceuticals and varnishes constituent and as raw material for optical glasses, among others (Peters et al., 2011).

2. State of the art

Carbon utilisation options are at different levels of technological development and market maturity, and in particular, CO_2 to produce chemicals and fuels are mostly at development phase. Methanol production is especially important in emerging economies, as a candidate liquid fuel to replace conventional source of energy. Methanol synthesis from captured CO_2 is being built at a commercial scale: Iceland, Japan and Korea have large scale pilot plants that combine carbon dioxide and renewable hydrogen (Quadrelli et al., 2011). Carbon Recycling International (CRI) started the operation of the first commercial demonstration plant, in Iceland, in 2011. There exist two catalytic routes to synthesize CH_3OH: direct hydrogenation with H_2 or CO_2 conversion into CO and further hydrogenation of CO (Van-Dal and Bouallou, 2012). As alternative, methanol can be also produced electrochemically by CO_2 reduction and H_2O oxidation. The electrochemical conversion of CO_2 can be customized to produce different products by appropriately selecting electrocatalysts, electrolytes and applied potential (Agarwal et al., 2011). Research is also in the line of mimicking photosynthesis, considering solar energy as the source for CO_2 reduction with H_2O in a compacted photo-electrochemical cell (Ampelli et al., 2011). The route considered in this work is the closest to the market, i.e. the catalytic route. *Hydrogen* for CH_3OH must be provided to the process in a carbon-free way to reduce the life cycle CO_2 emissions: H_2 from water electrolysis using a renewable source of electricity is considered as renewable. It may be produced through alkaline or proton exchange membrane electrolysis (PEM), while H_2 from steam electrolysis is produced via a solid electrolyser cell (SOEC). This last is the most efficient option, but this is currently the less developed (Redissi and Bouallou, 2013). Biomass, solar and wind are the most common renewable sources proposed for electricity supply in water electrolysis (Langè and Pellegrini, 2013): while wind is currently the most cost effective source among the renewable (Mignard and Pritchnard, 2008). *Mineralisation of CO_2* or *mineral carbonisation* mimics the natural weathering phenomenon, where natural alkaline silicate minerals and atmospheric CO_2 react. This process has however very slow kinetics. It can be accelerated (i) if the concentration of CO_2 is larger, (ii) if mineral has a larger reaction surface (grinding), (iii) if pressure is increased, and (iv) if moisture is present. Accelerated carbonation may use natural ore or alkaline solid waste to react with CO_2 (Huijgen et al. 2006). The process can take place ex-situ, in a chemical plant after mining and after mineral transportation, or after residue collection; or in-situ, by injecting CO_2 into appropriate geological formations and where the mineral matrix is not extracted from the mineral itself. Its main advantage is that it provides a permanent CO_2 storage (Montes-Hernandez et al., 2009). Experimental installations have been already carried out, using different types of rocks (that must be grinded) or industrial waste (that may be already at a reduced particle size), like Alcoa, Skyonic and Calera, Novacem and Calix at pilot plant or lab scales. Accelerated carbonation tolerates different degrees of CO_2 purity (GCCSI and PB, 2011). The conversion process selected for this work contemplates the utilization of fly ash from a coal power plant, which is already in a milled state.

3. Plants modelling

The boundaries of the current models are from "gate-to-gate": only the carbon re-use process is modelled. The CO_2 is captured from a power plant and then it is usually transported in a supercritical state, at 85-150 bar and 12-44 °C (EC, 2011). Considering transportation by on-shore pipeline, according to ZEP (2011), the delivery pressure is 61 bar, and the delivery temperature is around 10 °C, as the approximate ambient ground temperature. See in Table 1 the CO_2 average composition of the CO_2 stream, if pre-combustion, post-combustion and oxy-fuel capture methods are considered.

Table 1: CO_2 average composition, from coal and gas power plant, in % by volume (EC, 2011).

Component	% by volume
N_2/O_2	1.57
H_2S	0.05
H_2	0.40
SO_2	0.09
CO	0.04
CH_4	0.34
CO_2	97.51

Table 2: Size and working conditions for the selected technologies (Mineralisation: Montes-Hernández et al. 2009; Huijgen et al. 2006; DOE/NETL, 2013. Methanol synthesis: Van-Dal and Bouallou, 2012; Van-Dal and Bouallou, 2013; webpage of CRI, accessed 24.02.2014).

	Renewable methanol	Mineral carbonation
Plant size	1,300 (t of product/d)	14,400 (kg/h of fly ash)
Pressure (bar)	75.7 (Reaction) and 1.1 (Distillation)	20 (Reaction)
Temperature (°C)	210 (Adiabatic reactor)	30 (Isothermal reactor)
Mass flow of CO_2 (kg/h)	80,500	464 (Stoichiometric)
Mass flow of reactants (kg/h)	10,977 (Stoichiometric H_2)	216,000 of H_2O (L/S=15 kg/kg)

The models performed in this preliminary approach use CO_2 at a 100 % of purity, assuming a further process of purification after its transportation, whose modelling is beyond the scope of the current work. It is assumed that no by-products are produced. The employment of renewable sources for the provision of electricity in the water electrolysis process to produce H_2 is not taken into account: the electricity production (i.e. the CO_2 emissions) is from a pulverised coal power plant. Specifically for the case of aqueous carbonation, it is supposed that the conversion at large scale and with a continuous reactor, behaves as the experimental batch reactor used as reference. See in Table 2 the most representative average size, input data and working conditions for the selected plants. The models have been implemented in a process flow modeller. Thermodynamics properties are calculated with the property packages Redlich-Kwong-Soave and NRTL for low and high pressure sections in methanol synthesis, respectively, and Peng-Robinson for CO_2 mineralisation. The needed rules of thumb and costs expressions for conceptual design dimensioning and costs evaluation are from Towler and Sinnott, 2013.

3.1 Methanol production

The process simulated uses CO_2 already purified in combination with H_2 from water electrolysis, that consumes 4.8 kWh_{el}/Nm^3 of H_2 produced (Van-Dal and Bouallou, 2013). It is assumed that the plant produces 1,300 t/d of methanol. Therefore, according to the efficiency reported in Van-Dal and Bouallou, 2013, the corresponding inlet CO_2 stream is of 80,500 kg/h. Inlet H_2 correspond to the stoichiometric amount of H_2, according to the governing Eq(1):

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad (1)$$
$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad (2)$$

Eq(2) occurs in parallel reducing the amount of CO_2 converted into CH_3OH. The resulting water stream can be potentially recycled to the CO_2 capture plant to provide the needed water for the conversion of CO into CO_2, or used for electrolysis. Doped metal oxides are usually used as catalysts for Eq(1). The implemented kinetics correspond to those using the catalyst $Cu/ZnO/Al_2O_3$: specific reaction rates expressions can be found in Van-Dal and Bouallou (2013), and they follow the Langmuir-Hinshelwood-Hougen-Watson model.

See in Figure 1 a simplified block diagram of the model. CO_2 is entering from the capture plant at 1.1 bar. H_2 is coming from the electrolysis process at 30 bar. Both streams are at 25 °C. They are compressed separately until 78 bar. The CO_2 compressor is multistage according to the same P_i/P_{i-1} ratio for each stage, along with $(P_n/P_o)^{1/n}$ close to 2.5, where P_n and P_o are the initial and final pressures, respectively. Therefore, three stages have resulted for CO_2 and one stage compressor for H_2. Then, the mixture of both streams is heated up until the temperature of the methanol reactor (210 °C): this is an adiabatic fixed bed reactor simulated by a kinetic plug-flow reactor. Reactor dimensions have been calculated for the case study described in Van-Dal and Bouallou, 2013 and taken into account the amount (44,500 kg) and density (1,775 kg/m^3) of the utilised catalyst, resulting in a diameter of 2.13 m and a height of 8.5 m. Final height is 7.9 m for the inlet conditions of the current case study, to maintain the same conversion. HE1 heats up the mixture of CO_2 and H_2 while cooling down the appropriate amount of products resulting in the methanol reactor (from 286.5 °C until 92 °C). The conditioning system adapts the mainly CH_3OH and water stream to 35 °C and 73.4 bar. The heat exchanger is integrated downstream with HE2 and the reboiler heating needs. Flash1 separates the mixture, with a vapour fraction of 0.904. CO_2 recycling injects the resulting CO_2 stream into the inlet mixture of CO_2 and H_2. COMP3 increases the pressure again until 78 bar. Then, the distillation column that separates methanol and water has as inlet conditions 80 °C and 1.1 bar. Flash2 separates any vapour fraction before methanol purification. The detailed model for the distillation column counts with 57 stages, a reflux ratio of 1.2, and a bottoms-to-feed ratio of 0.4, in mole basis. Feed stream is on stage 44. Further purification is obtained with the following COMP4 and HE3, finally delivering CH_3OH at atmospheric pressure and 20 °C. The ΔP considered in all heat exchangers take is of 0.2-0.3 bar. Compressors consider a mechanical efficiency of 0.8. If not mentioned the integration of streams, the
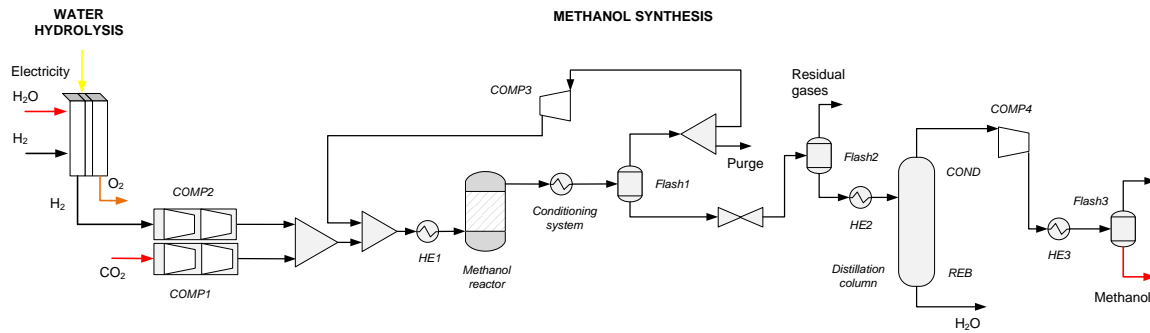
Figure 1: Simplified simulation flowsheet of methanol synthesis produced from captured CO_2 and H_2 from water electrolysis (own source and model based on Van-Dal and Bouallou, 2012)

heat exchanged is with water at 1.1 bar and 25 °C. The electricity provided by the coal power plant adds 803 tCO_2/GWh (DOE/NETL, 2013) to the overall CO_2 balance.

Reactor simplification: The results of the kinetic methanol reactor for different flowrates have been analysed in order to simplify its implementation. By adjusting the amount of methanol synthesized, it is possible to replace the kinetic reactor by an equilibrium reactor at the temperature $T_{reactor}$ + *13.85 °C*, with an error of +/-3-5% in composition and temperature.

3.2 Accelerated aqueous carbonation of fly ash

The process receives the CO_2 already purified and the fly ash from the baghouse of a 550 MW_e pulverised coal power plant (DOE/NETL, 2013). It is assumed that the plant utilises the fly ash collected in the abovementioned power plant: 14,400 kg/h. The inlet amount of CO_2 is 464 kg/h, according to the stoichiometry of Eq(3) and Eq(4):

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{3}$$
$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{4}$$
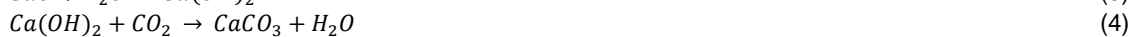
Where, CaO is a 4.1 % on a mass basis; being the rest of the components 50 % of SiO_2, 30 % of Al_2O_3, and 15.9 % of Fe_2O_3 (Montes-Hernandez et al., 2009). The resulting water stream, that now is not recycled to form the slurry, can be used for other heating/cooling purposes (T = 40 °C), or potentially recycled to the CO_2 capture plant to provide the needed water for the water gas shift reactor. Fly ash, further grinded (if needed) and suspended in water, reacts in the carbonation reactor according to a pseudo-second-order kinetic model, dependent on CO_2 concentration, for Eq(4) (Montes-Hernandez et al., 2009).

See in Figure 2 a schematic block diagram of the model. CO_2 is entering from the capture plant, and fly ash is entering from the same power plant, at 1.1 bar and 25 °C. H_2O is also entering at the same conditions of P and T, with a corresponding flowrate of 15 times the flowrate of fly ash, according to the ratio liquid / solid (L/S=15kg/kg) (Huijgen at al., 2006). CO_2 is compressed until at least 20 bar, that is the
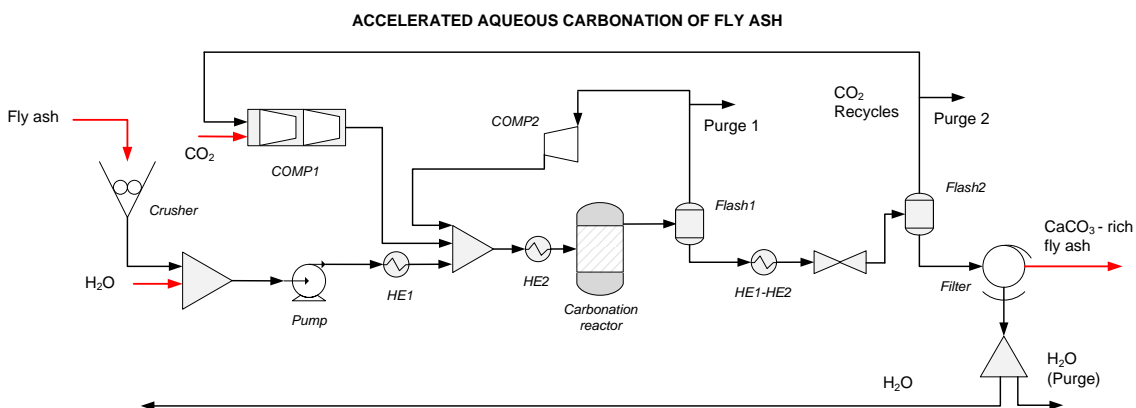

Figure 2: Simplified simulation flowsheet of accelerated and aqueous carbonation of fly ash from a coal power plant - own source and model based on Huijgen at al. (2006) and Montes-Hernandez et al.(2009).

inlet pressure of the carbonation reactor. A multistage compressor (with two stages) is used, analogously to the previous model. Fly ash slurry is pumped at the same pressure. Fly ash is previously grinded until a maximum of 40 μm (Bond working index = 12 kWh/t). HE1-HE2 cools down the liquid product of the carbonation reactor reaching 40 °C and 17.9 bar, while conditioning the reactor inlet stream (if needed). The valve expands the product till atmospheric pressure for separation. If necessary, CO_2 can be recycled at two points of the flowsheet (in units flash1 and flash2, after reaction and expansion). A centrifuge filter, working at 1,200 rpm is selected to separate solids and liquids. The carbonation reactor has been divided into two reactors for modelling purposes: one stoichiometric reactor that reaches the complete conversion of CaO into $Ca(OH)_2$ (Eq(3)) and a kinetic reactor with the following preliminary adaptation of the kinetic rate expression described in Montes-Hernandez et al. 2009, taking into account that the volume of reaction is 1 dm^3: $rate_{CaCO3}[mol/m^3s] = 0.4877*(0.032-[CaCO_3])$. The whole ΔP is of 1.5 bar. Again, the ΔP considered in all heat exchangers is between 0.2-0.3 bar. Compressors have a mechanical efficiency of 0.8. If not mentioned the integration of streams, the heat exchanged is with water at 1.1 bar and 25 °C. A coal power plant releases 803 tCO_2/GWh (DOE/NETL, 2013).

Reactor simplification: The reactor has been replaced by a stoichiometric reactor that calculates the consumed moles of CO_2 according to the behaviour observed in Montes-Hernandez et al. (2009): the carbonation efficiency CaO-$CaCO_3$ is approximately 82 %. Therefore, the reactor calculates the n_{CaCO3} = $n_{Ca(OH)2}$ [mol/h] = 0.82*m_{CaO} [kg/h] / 56.077. This carbonation efficiency has been checked at different larger rates than experimental, and the error is around +/-0.5-1 % compared to the results obtained with the kinetic reactor.

4. Results

The results, represented as a list of key performance indicators (KPI) for both processes, are shown in Table 3. (i) Product purity refers to the % on a mass basis of CH_3OH and $CaCO_3$ in the product stream for both processes. (ii) The % of CO_2 converted in the reactor is a ratio between the outlet/inlet molar flow.

(iii) The CO_2 recycled and converted expresses the percentage of CO_2 that is not released of the system, i.e. the CO_2 that has been used or recycled. (iv) The selectivity is only expressed for the methanol reactor, since two different reactions using CO_2 are taking place; on the contrary, in mineral carbonation only the mineralization reaction is considered in the reactor. (v) Heat duty and (vi) electricity duty expresses the utility needs per ton of CO_2 used. (vii) CO_2 emissions in CO_2 emissions per ton of CO_2 used, refers to the emissions corresponding to outlet streams from the two processes described, plus the CO_2 released due to the production of the electricity need. And finally, the (viii) CAPEX is the total investment required (including contingencies) per ton of CO_2 used, following Hand's method. This estimation corresponds to a preliminary estimate, so the accuracy is typically +/- 30 %. The estimated costs, as a starting value, assume that the only material used is carbon steel. For the estimation of heat exchangers costs, heat interchange with water or steam is assumed (Towler and Sinnott, 2013). Even if the purpose of this work is not to compare the two CCU options among them, since different needs are satisfied by the two differentiated processes, is it important to remark that mineralisation is more advantageous in terms of electricity needed and relative CO_2 emissions, while methanol production is cheaper in relative terms, and more efficient, in general. Its absolute CAPEX is 150 MEUR, while the absolute CAPEX for mineralisation is 25 M€.

Table 3: List of KPIs evaluated for each methanol synthesis and carbon mineralisation.

KPIs	Renewable methanol	Mineral carbonation
Product purity (%wt)	88 (of CH_3OH)	6 (of $CaCO_3$)
CO_2 converted in the reactor (%)	27	17
Total CO_2 recycled and converted (%)	94	82
Selectivity	33.7	-
Heat duty (MWh/tCO_2used)	1.47 (cooling needs)	1.57 (cooling) , 8.18 (heating)
Electricity requirement (MWh/tCO_2used)	8.08	1.28
CO_2 emissions (tCO_2/tCO_2used)	6.5 (0.3 without electrolysis)	1.3
CAPEX ($MEUR_{2010}/(tCO_2$used/h))	1.98	65.5

5. Conclusions

The analysis presented in this work considers methanol production and accelerated aqueous carbonation of fly ash for carbon re-use. The two conceptual designs, at realistic scales, have been simulated in order to obtain the needed mass and energy balances to evaluate the KPIs. This paper describes the methodology followed and that will be also applied for studying other CCU technologies, with the final purpose of performing a global market study that focuses on (i) current prices and demands for the CO_2 products, and (ii) the analysis of their foreseen market evolution and price elasticity. The study aims to indicate the most sustainable ways to convert CO_2 and analyse the role of CCU in the whole CCUS context. Further this work may also help on prioritizing support and/or RD&D funding to enable the commercialisation of the selected CCU technologies.

References

Ampelli C., Passalacqua R., Genovese C., Perathoner S., Centi G., 2011, A novel photo-electrochemical approach for the chemical recycling of carbon dioxide to fuels, Chemical Engineering Transactions, 25, 683-688.

Agarwal A., Zhai Y., Hill D., Sridhar N., 2011, The electrochemical reduction of carbon dioxide to formate/formic acid: Engineering and economic feasibility, ChemSusChem, 4, 1301-1310.

Aresta M., Dibenedetto A., Angelini A., 2013, The changing paradigm in CO_2 utilisation, Journal of CO_2 Utilisation, 3-4, 65-73.

Boot-Handfort M.E., Abanades J.C., Anthony E.J., Blunt M.J., Brandani S., Mac Dowell. N., Fernández J.R., Ferrari M.-C., Gross R., Hallet J.P., Haszeldine R.S., Heptonstall P., Lyngfelt A., Makuch Z., Mangano E., Porter R.T.J., Pourkashanian M., Rochelle G.T., Shah N., Yao J.G., Fennell P.S., 2014, Carbon capture and storage update, Energy Environ. Sci., 7, 130-189.

Department of Energy / National Energy Technology Laboratory, 2013, Cost and performance baseline for fossil energy plants. Volume 1: Bituminous coal and natural gas to electricity. Revision 2a.

European Commission (EC), Joint Research Centre Scientific and Technical Reports, 2011, Technical and economic characteristics of CO_2 transmission pipeline infrastructure. <publications.jrc.ec.europa.eu/repository/> accessed 28.02.2014

Global CCS Institute and Parsons Brinckerhoff (GCCSI and PB), 2011, Accelerating the uptake of CCS: Industrial use of captured carbon dioxide. <www.globalccsinstitute.com/publications> accessed 28.02.2014

Huijgen W.J.J., Jan Ruijg G., Comans R.N.J., Witkamps G-J., 2006, Energy consumption and net CO_2 sequestration of aqueous mineral carbonation, Ind. Eng. Chem. Res., 45, 9184-9194.

Langè S., Pellegrini L.A., 2013, Sustainable combined production of hydrogen and energy from biomass in Malaysia, Chemical Engineering Transactions, 32, 607-612.

Mignard D., Pritchard C., 2008, On the use of electrolytic hydrogen from variable renewable energies for the enhanced conversion of biomass to fuels, Chemical Engineering Research and Design, 86, 473-487.

Montes-Hernandez G., Pérez-López R., Renard F., Nieto J.M., Charlet L., 2009, Mineral sequestration of CO_2 by aqueous carbonation of coal combustion fly-ash, Journal of Hazardous Materials, 161, 1347-1354.

Peters M., Köhler B., Kuckshinrichs W., Leitner W., Markewitz P. Müller T., 2011, Chemical technologies for exploiting and recycling carbon dioxide into the value chain, ChemSusChem, 4, 1216-1240.

Quadrelli E., Centi G., Duplan J.-L., Perathoner S., 2011, Carbon dioxide recycling: emerging large-scale technologies with industrial potential, ChemSusChem, 4, 1194-1215.

Redissi Y., Bouallou C., 2013, Valorization of carbon dioxide by co-electrolysis of CO_2/H_2O at high temperature for syngas production, Energy Procedia, 37, 6667-6678.

Towler G., Sinnott R.K., 2013, Chemical engineering design. Principles, practice and economics of plant and process design, BH, Elsevier, Massachussets, USA.

Van-Dal E.S., Bouallou C., 2012, CO_2 abatement through a methanol production process, Chemical Engineering Transactions, 29, 463-468.

Van-Dal E.S., Bouallou C., 2013, Design and simulation of a methanol production plant from CO_2 hydrogenation, Journal of Cleaner Production, 57, 38-45.

Zero Emissions Platform (ZEP), 2011, The costs of CO_2 transport. Post-demonstration CCS in the EU. Downloaded at <www.zeroemissionsplatform.eu/library> accessed 28.02.2014