

Plasma assisted conversion of hydrocarbons for a green and environmental friendly energy transition

laurent.fulcheri@mines-paristech.fr

PERSEE Centre Procédés, Energies Renouvelables et Systèmes Energétiques



Outline

- Context
- Overview of Potential contribution of plasmas
- Thermodynamics
- Reforming / Gasification
- Direct Decarbonization of Methane for the co-production of CB & H₂
- Summary

Context

- Fossil fuels depletion (conventional)
- Increase of demography
- **Global Warming** and other environmental impacts : NOx, COv, particles,...
- Total worldwide anthropic emissions: 36 10⁹ tons CO₂ eq. (80 % fossil fuel combustion)

Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica

J. R. Petit*, J. Jouzel†, D. Raynaud*, N. I. Barkov‡, J.-M. Barnola*, I. Basile*, M. Bender§, J. Chappellaz*, M. Davisl, G. Delaygue†, M. Delmotte*, V. M. Kotlyakov5, M. Legrand*, V. Y. Lipenkov‡, C. Lorius*, L. Pépin*, C. Ritz*, E. Saltzmanl & M. Stievenard†

* Laboratoire de Glaciologie et Géophysique de l'Environnement, CNRS, BP96, 38402, Saint Martin d'Hères Cedex, France

† Laboratoire des Sciences du Climat et de l'Environnement (UMR CEA/CNRS 1572), L'Orme des Merisiers, Bât. 709, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France ‡ Arctic and Antarctic Research Institute, Beringa Street 38, 199397, St Petersburg, Russia

§ Department of Geosciences, Princeton University, Princeton, New Jersey 08544-1003, USA

Rosenstiel School of Marine and Atmospheric Science, University of Miami, 4600 Rickenbacker Causeway, Miami, Florida 33149, USA § Institute of Geography, Staromonetmy, per 29, 109017, Moscow, Russia



Factor 4



• The European Union has formulated the ambition to cut CO₂ emissions by 80% in 2050 (factor 4)

Energy sector

- The need and urgency to create a sustainable energy future is spurring innovation in the energy sector.
- A multi-B€ energy technology market has emerged driven by investors and researchers.
- Countries like China, Germany, Japan and the USA invest heavily in green energy technology.
- RE powered by the sun including photovoltaic, concentrated solar, hydro, wind, biomass will definitively contribute significantly to the energy supply mix of 2025

But...

- Main limitation to large-scale deployment are:
 - Cost of RE technologies
 - **Supply-demand** matching
 - Not suitable for mobile applications (cars, boats, planes,...)
- To overcome these limitations Storage and transport must be considered as an integral part of future energy system

Energy storage

Mass required to store the equivalent of one kg of oil (11,6 kWh - 1,3 litre - 0,55 US gallon)

Wood	Lead-acid batteries	Compressed H ₂	Water in altitude	Heat
2,22 kg exclusive use of a couple of m ² of land over a year	300 kg of batteries	a tank weighting 15 to 30 kg , with an inside capacity of 30 litres	43 tons of water able to fall from 100 m	10 °C of temperature rise for 1 ton of water

- Provided the conversion of electricity into Synthetic Fuel can be done efficient and cost effective, green SF are expected to become a major primary energy storage.
- Green SF will be one of the solutions to the imbalance between supply and demand of RE electricity generation.
- Suitable for **mobile** applications.

Options ?

- Short-middle term: Fuels decarbonization
 - #0 Capture & Sequestration
 - #1 Biomass
 - #2 CO₂ retro-conversion
 - #3 Direct Decarbonization of fossil fuels
- Longer term: Solar fuels direct from CO₂ and H₂O





Overview of potential contribution of plasmas



Thermodynamics basis = CH_4

	Standard enthalpy of formation (kJ.mole ⁻¹)		
CO ₂	-393,52		
$H_2O_{(I)}$	-285		
$H_2O_{(g)}$	-241		
$CH_3OH_{(I)}$	-238		
СО	-110,58		
CH ₄	-74,9		
H ₂	0		
O ₂	0		
C _(s)	0		

Combustion (total oxidation)

- $CH_4 + 2O_2$
- $C + O_2$
- $H_{2} + \frac{1}{2}O_{2}$
- $CO + \frac{1}{2}O_2 \rightarrow CO_2$
- $CH_3OH + 3/2 O_2 \rightarrow CO_2 + 2H_2O_{(1)}$

- \rightarrow CO₂ + 2H₂O₍₁₎
- \rightarrow CO₂
- \rightarrow H₂O₍₁₎

- -888 kJ.mole⁻¹
- -393 kJ.mole⁻¹
- -285 kJ.mole⁻¹
- -283 kJ.mole⁻¹
- -725 kJ.mole⁻¹

During the combustion of methane : 40 % of the NRJ comes from Carbon (bad boy) while 60 % comes from Hydrogen (good boy)

Thermodynamically speaking 1 mole H₂ almost equivalent to 1 mole CO (Δ H (WGS) ~ 0)

Partial oxidation (Gasification / Reforming)

- $CH_4 + \frac{1}{2}O_2$
- $CH_4 + CO_2$
- $CH_4 + H_2O_{(I)}$
- $\rightarrow CO + 2H_2$ $\rightarrow 2CO + 2H_2$ $\rightarrow CO + 3H_2$
- -35 kJ.mole⁻¹ +248 kJ.mole⁻¹ +250 kJ.mole⁻¹

Highly endothermic except POx Steam and Dry Reforming almost equivalent

Cracking – decomposition – reduction

- CH_4 \rightarrow $C + 2H_2$ +75 kJ.mole⁻¹ (1.736 kWh.kg⁻¹ carbon)
- $H_2O_{(1)}$ $\rightarrow H_2 + \frac{1}{2}O_2$ +285 kJ.mole⁻¹ • CO_2 $\rightarrow CO + \frac{1}{2}O_2$ +283 kJ.mole⁻¹

H₂ production from DMD (38 kJ.mole⁻¹ H₂) is thermodynamically 8 times less costly than from liquid Water Splitting (285 kJ.mole⁻¹ H₂)

 H_2 production from DMD (38 kJ.mole⁻¹ H_2) is thermodynamically less costly than SR (62 kJ.mole⁻¹ H_2 eq.)

Reduction of H₂O to H₂ and CO₂ to CO are thermodynamically equivalent

Synthesis

Methanation (Sabatier)

• $CO + 3H_2$ $\rightarrow CH_4 + H_2O$ -250 kJ.mole⁻¹ • $CO_2 + 4H_2$ $\rightarrow CH_4 + 2 H_2O$ -252 kJ.mole⁻¹ Methanol • $CO + 2H_2$ $\rightarrow CH_3OH$ -128 kJ.mole⁻¹

All exothermal (idem for all FT)

The two methanation pathways are thermodynamically equivalent (CO vs CO₂)

Plasma chemistry (Thermodynamic equilibrium)

C:H

2 000 K – 5 000 K 1 atm ~ 13 species (neutral only)

C, C₂, C₃, Cs, H, H₂, CH, C₂H, C₃H, C₄H, CH₂,C₂H₂ ,C₄H₂ + ions + excited species + electrons

C:H:O

2 000 K - 5 000 K 1 atm ~ 24 species (neutral only)

C, C₂, C₃, Cs, H, H₂, CH, C₂H, C₃H, C₄H, CH₂,C₂H₂, C₄H₂ + CHO, CHO₂, CH₂O, CH₂O₂, CO, CO₂, HO, H₂O, H₂O₂, O, O₂ + ions + excited species + electrons



Reforming Gasification



Context

- On board reforming
- Transition solution: Fossil
 direct H₂
- Existing infrastructures
- Collaboration with RENAULT
- 3 successive Ph.D (Rollier 2006, Petitpas 2008, Lebouvier 2011)
- PLASMA
 - Alternative to heterogeneous catalysis
 - Compactness
 - Dynamic response
 - Limited poisoning sensibility
 - Flexibility regarding the fuel composition



Experimental bench

ARTICLE

nubs acs oro/FE







Reactive Diesel fuel evaporator injection

Postreactor

INSTITUTE OF PHYSICS PUBLISHING Plasma Sources Sci. Technol. 16 (2007) 183-192

Design and electrical charaterization of a low current-high voltage compact arc plasma torch

L Fulcheri, J-D Rollier and J Gonzalez-Aguilar



E-mail: laurent.fulcheri@ Received 17 May 200 Published 20 Decemb Online at stacks.iop.o

Centre for Energy and Pro

Exhaust Gas Fuel Reforming of Diesel Fuel by Nonthermal Arc Discharge for NO_x Trap Regeneration Application

Alexandre Lebouvier,^{†,#} François Fresnet,[#] Frédéric Fabry,[†] Valérie Boch,[#] Vandad Rohani,[†] François Cauneau,⁺ and Laurent Fulcheri*'

*Center for Energy and Processes, MINES ParisTech, Rue Claude Daunesse BP 207, 06904 Sophia Antipolis Cedex, France *Technocentre Renault, Direction de la Recherche, des Etudes Avancées et des Matériaux DREAM/DTAA - Service 68240, 1 avenue du golf, 78288 Guyancourt Cedex, France

PLASMA SOURCES SCIENCE AND TECHNOLOGY

doi:10.1088/0963-0252/16/1/023

Plasma technology

- Low current High voltage helical arc
- Resonance power supply
- Pre mixed injection (gas phase)



JOURNAL OF PHYSICS D: APPLIED PHY

Time = $0.000500 \, s$



1889

IEEE TRANSACTIONS ON PLASMA SCIENCE, VOL. 39, NO. 9, SEPTEMBER 2011

Three-Dimensional Unsteady MHD Modeling of a Low-Current High-Voltage Nontransferred DC Plasma Torch Operating With Air

> Alexandre Lebouvier, Clarisse Delalondre, Francois Fresnet, Valerie Boch, Vandad Rohani, Francois Cauneau, and Laurent Fulcheri

IOP PUBLISHING J. Phys. D: Appl. Phys. 45 (2012) 025204 (9pp)

3D MHD modelling of low current-high voltage dc plasma torch under restrike mode

A Lebouvier^{1,2}, C Delalondre³, F Fresnet², F Cauneau¹ and L Fulcheri¹

¹ Center for Energy and Processes-MINES ParisTech, Rue Claude Daunesse, 06904 Sophia Antipolis, France

² Technocentre Renault, DREAM/DELT'A, 78288 Guyancourt, France
 ³ EDF R&D, MFEE Department, 6 quai Watier, 78400 Chatou, France
 E-mail: laurent fulcheri@mines-paristech.fr

Received 9 September 2011, in final form 24 November 2011 Published 20 December 2011 Online at stacks ion org/(Phys.D)(45/025204

Experiments

- Fuels: Gasoline, Ethanol, E85, Diesel
- Main investigated parameters:

Nozzle geometry

-O/C, H_2O/C , input power, Flow rate

$$\eta_{ener} = \frac{Q_{H2} \times LHV_{H2} + Q_{C0} \times LHV_{C0}}{Q_{fuel} \times LHV_{fuel} + P} \leftarrow P = \text{Net plasma power}$$

	Methane	Gasoline	Ethanol
Partial oxidation	-35.7 kJ/mol	-675 kJ/mol	14 kJ/mol
Steam reforming	206 kJ/mol	1258 kJ/mol	256 kJ/mol

Ethanol





Conversion rate () and energy efficiency ()





Received January 6, 2010. Revised Manuscript Received March 8, 2010

POx Diesel (optimized system)



1D-Kinetic Modelling



Hydrocarbons : n-octane, methane, ethanol, E85, gazole, ...



Results (n-octane)



2D-CFD-Kinetic Modelling



Results (diesel)

Reduced N-Heptane kinetic mechanism 41 reactions



energy&fuels ARTICLE

pubs.acs.org/EF

2D Axisymmetric Coupled Computational Fluid Dynamics-Kinetics Modeling of a Nonthermal Arc Plasma Torch for Diesel Fuel Reforming

Alexandre Lebouvier, François Cauneau, and Laurent Fulcheri*

Center for Energy and Processes (CEP), MINES ParisTech, Rue Claude Daunesse BP 207, 06904 Sophia Antipolis Cedex, France

Direct *Decarbonization* of Methane for the co-production of CB & H₂



CO₂ emissions of present H₂ production technologies



Source DOE, 2013, Hydrogen production

Industrial context

Hydrogen

- Ultimate form of decarbonized energy
- Total world production: 60 Millions tons per year (NH₃ & oil industry)
- 5% annual growth
- 95% produced from fossil fuels (most methane SR)
- 12 kg CO₂ eq. per kg of H₂
- 720 Millions tons CO₂ eq. per year
- 2.25% of the Total worldwide emissions !!! (32 GT CO₂ eq. per year)

Carbon Black

- Total world production: 10 Millions tons per year (90% tire industry)
- 95% produced with furnace process (incomplete combustion heavy hydrocarbons)



- 4 kg CO₂ eq. per kg of CB
- 40 Millions tons CO₂ eq. per year
- 0.125% of the Total Worldwide Emissions (32 GT CO₂ eq. per year)

New Plasma Process



Int. J. Hydrogen Energy, Vol. 20, No. 3, pp. 197–202, 1995 Copyright © 1995 International Association for Hydrogen Energy Elsevier Science Ltd 0360–3199(94)E0022–Q Printed in Great Britain. All rights reserved 0360–3199/95 \$9, 50 + 0.00

FROM METHANE TO HYDROGEN, CARBON BLACK AND WATER

L. FULCHERI and Y. SCHWOB

Centre d'Energétique, Ecole des Mines de Paris, 06560 Sophia-Antipolis, France

(Received for publication 11 March 1994)

Abstract-Most of the total world production of hydrogen comes from vapor cracking of methane. Even though methane is the least carbogen of all hydrocarbons, steam conversion of one ton of methane is accompanied by the emission of about four tons of CO_2 into the atmosphere. Simple thermolysis of methane being no more endothermic than the vapor cracking reaction, cracking methane without any oxygen into carbon and hydrogen should, theoretically, be no more energy-expensive than existing processes. To be effective, such a thermolysis needs a very high temperature reaction which, with recent improvements in plasma technology, is now accessible. The main advantage of carrying out thermolysis at high temperature is that, while producing hydrogen, reaction conditions may also be favourable for carbon black production. From physical considerations related to existing processes, the authors present a theoretical study which could open the way to new *plasma-assisted* processes.

More anecdotally, a certain number of natural gas resources remain unexploited due to their isolation; it is theoretically possible to transform these resources into carbon and water without any external energy supply. It would then be possible to irrigate the desert while producing a solid state product whose transport may be easier than gas.

1993...2006 : 5 worldwide Patents

Principle – Stakes

- $CH_4 \rightarrow C + 2H_2$
- Replacement of an incomplete combustion by the thermal decomposition of Methane into CB $\&~{\rm H_2}$
- Zero CO₂
- 100% carbon yields
- Co synthesis of two valuables chemicals
- New CB grades



What is Carbon Black ?

- > 97% elemental carbon
- BUT not "just CARBON" !!
- Contrary to Hydrogen it's mostly a Specialty not a Commodity



- More than 44 grades in the ASTM classification (for rubber applications only)
- 9 groups depending on the typical average primary particle size (nm)
 - 0-10
 - 11-19
 - 20-25
 - ...
 - 201-500
 - 2 main parameters
 - Iodine Adsorption (Surface Area)
 - ➔ primary particle size
 - Oil Adsorption
 - → Structure of Aggregate

Challenges

- Production of commercial CB grades
- Technology
- Energy Input
- The Arker Kvaerner experience (~ 60 M\$)
 - Researches initiated at SINTEF (Norway) in the 90's
 - Plasma technology : DC Hollow cylindrical graphite electrodes
 - 1995 : 1 MW Pilot in Hofors (Sweeden)
 - 1997-1998 : KARBOMONT Industrial plant with 20 000 tons CB capactity and 50 million normal cubic metres of $\rm H_2$
 - Never went into commercial exploitation
 - 2003 : STOP-DEMOLITION : Technical problems + Inability to produce commercial CB grades

Mines-ParisTech Technology



3-phase AC arcs



Plasma Reactor



Power: 250 kW Capacity: 20 kg/h Lining: graphite

Diagnostics

- U, I, P
- Pyrometry
- Emisssion Spectroscopy
- Calorimetry
- Mobile probes
- GC, GC-MS, IR
- Ultra fast camera

Key processing parameters

- Temperature history (enthalpy)
- Characteristics times:
 - Nucleation:
 - Particle formation:
 - Aggregate:
 - Ageing (PAH removing):
- → ultra fast H₂ Plasma-cold CH₄ mixing
- → control of temperature history



Plasma zone modelling



Plasma Chem Plasma Process (2013) 33:491-515 DOI 10.1007/s11090-013-9438-8

ORIGINAL PAPER

3D Unsteady State MHD Modeling of a 3-Phase AC Hot Graphite Electrodes Plasma Torch

Christophe Rehmet · Vandad Rohani · François Cauneau · Laurent Fulcheri

Results

- Demonstration of the ability to produce a wide range of commercial CB grades
- 100% carbon yields
- 100% H₂ yields
- 50 < BET < 120
- 90 < DBP < 250

Covering a wide range of industrial CB grades

- Very high reliability of the 3-phase AC plasma technology
- Hot consumable graphite electrodes technologies are particularly suitable for this application involving hydrogen plasma. They present unquestionable advantages versus other "classical" plasma technologies (DC, ICP, MW) in terms of reliability CAPEX and OPEX

Carbon Black



Global balances (1 ton CB)



Short term perspective

Currently building a large CB&H₂ demonstration plant with a technology largely inspired from MPT technology

Long term perspectives



- Regarding Clean H₂ production only
 - Even if DMD requires 1.2 to 1.7 kWh per Nm³ H₂ it remains much better than water electrolysis which requires 4 to 6 kWh per Nm³ H₂
 - It represents a real alternative versus the current SR (zero direct CO₂ vs 12 tons_{CO2} / ton_{H2})
 - One of the most credible breakthrough alternative technology compatible with the \$2/kgH₂ DOE objective

Summary

- In parallel with the development of Renewable Energy, Plasma processes can/will significantly contribute to the clean energy transition
- Chemical energy storage
 - Hydrogen
 - Syngas
 - Synfuels

Direct Methane Decarbonization (DMD)

- New context (shale gas)
- Co synthesis of CB & H_2
- Lower cost than water electrolysis
- Real alternative to Steam Reforming (CO₂)
- CO₂ retro-conversion

