TyGRe—High added value materials from waste tyre gasification residues

DR. ALPER SARIOĞLAN
TUBITAK MAM Energy Institute

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Russian Gubkin State University of Oil and Gas
Moscow – RUSSIA

PRESENTATION OF TUBITAK MRC EI

TÜBİTAK

The Scientific and Technological Research Council of Turkey (TÜBİTAK) is the leading agency for management, funding and conduct of research in Turkey.

It was established in 1963 with a mission to advance science and technology, conduct research and support Turkish researchers.

TÜBİTAK is responsible for promoting, developing, organizing, conducting and coordinating research and development in line with national targets and priorities.

TÜBİTAK reports directly to the Prime Minister and acts as an advisory agency to the Turkish Government on science and research issues, and is the secretariat of the Supreme Council for Science and Technology (SCST), the highest S&T policy making body in Turkey.

Organization Chart of TÜBİTAK

Science Board

President

Vice President	Vice President	Vice President	IN-HOUSE RESEARCH
Academic R&D Funding Directorate	Science and Technology Policy Department	International Cooperation Department	• Marmara Research Center • National Research Institute of Electronics and Cryptology • Basic Sciences Research Institute • Defense Industries R&D Institute •Çukurova Advanced Agro-Technology Res.Inst. • Space Techn.Res.Institutes
Industrial R&D Funding Directorate	Science in Society Department		

Marmara Research Center

The Scientific and Technological Research Council of Turkey (TÜBİTAK) Marmara Research Center (MRC), one of the research and development units of TÜBİTAK, was established in 1972.

With the vision of "taking part among the leading science and technology centers of the world in the field of applied research" and the mission of "contributing to the development of Turkey’s competing power, using science and technology", TÜBİTAK MRC looks forward to developing close relationship with Turkish industry.

Organizational Structure

TUBITAK

(The Scientific and Technological Research Council Of Turkey)

TUBITAK MRC (Marmara Research Center)

TUBITAK MRC Energy Institute (EI)

EI Staff Profile

Management	**3**
Researcher	**99**
PhD	20
MSc	54
BSc	25
Technician	**34**
Support	**4**
Total	**140**

Main Characteristic of Staff Profile:
Multidisciplinary (Engineers of Mechanics, Electronics,Chemistry, etc.)
Deep expertise seniors & innovative researchers.

Energy Institute Working Areas

Strategic Bussiness Units

***1.Advanced Energy Technologies*:**

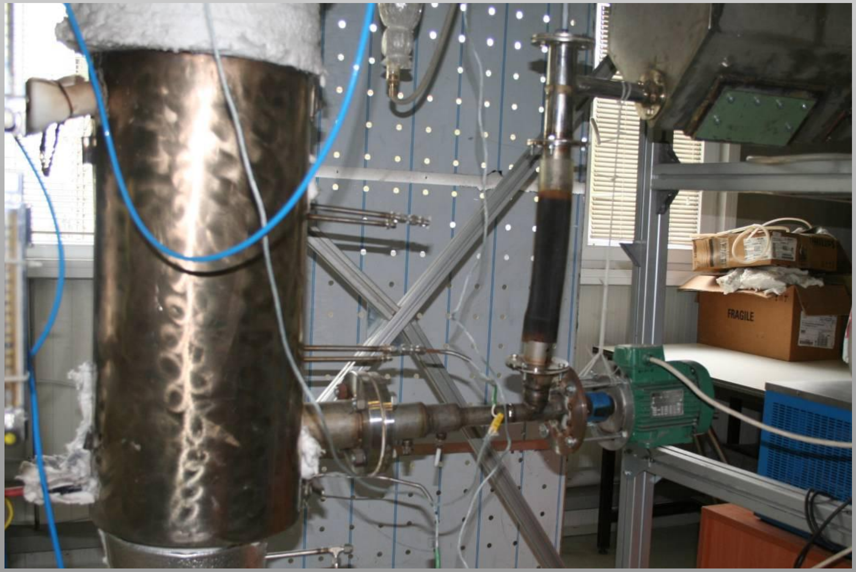
- **Fuel Cell Technologies (PEMFC, DSBHFC)**
- **Hydrogen Production (NG and Diesel) and storage**
- **Combustion, Gasification and Gas Cleaning technologies**
- **Fuel Technologies**

***2. Power Electronics and Control Technologies*:**

- **Power Electronics Technologies**
- **Vehicle Technologies**
- **Battery Technologies**

GASIFICATION PLANTS AT TUBITAK MRC EI

WASTE TIRE GASIFICATION TEST RIG AT TUBITAK MRC EI



TYGRE PROJECT

TYGRE-High Value Added Materials from Waste Tire Gasification Residues

FP7-ENV-2008-1 Collaborative Project

(01 September 2009 – 01 March 2013)

TYGRE PROJECT PARTNERS

- Ente per le Nuove tecnologie, l’Energia e l’Ambiente (ENEA) – Coord.
- TÜBİTAK Marmara Research Center Energy Institute
- European Tyre Recycling Association (ETRA)
- Rheinisch-Westfälische Technische Hochschule Aachen (RWTH)
- ELASTRADE
- Institute of Materials and Environmental Chemistry (IMEC)
- Febe Ecologic
- Copenhagen Membrane Technology A/S (COMETAS)
- SICAV S.r.l

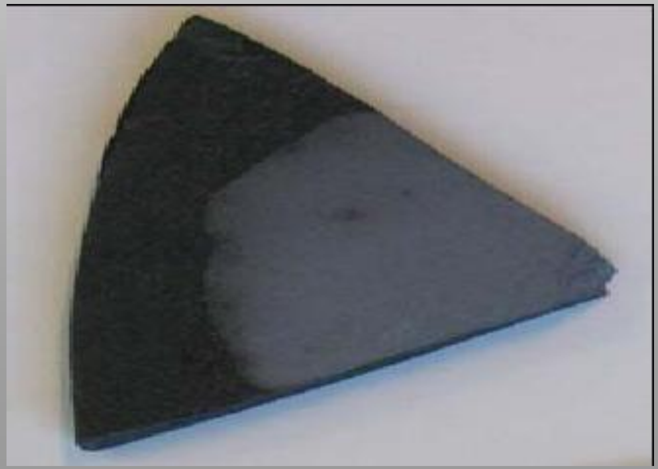
THE REASONS BEHIND THE PROJECT IDEA

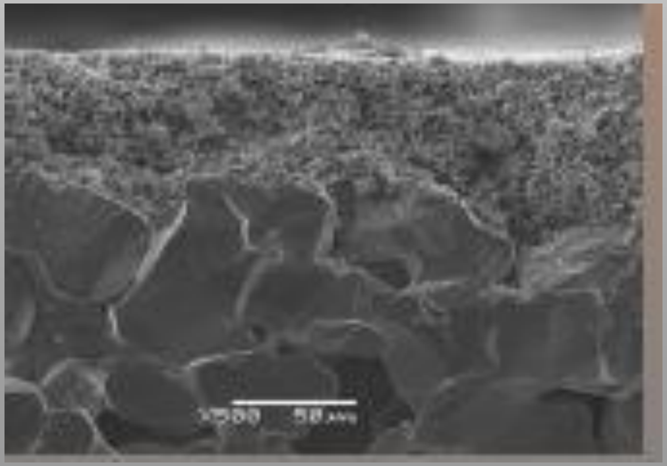
Current European Union Regulations promote the recycling of wastes. In this direction, TYGRE Project aims at production of silisium carbide with the reaction of silisium oxide and carbon residue left after gasification.

$$SiO_2(s) + 3C(s) \leftrightarrow SiC + 2CO$$

$$SiO_2 + C \leftrightarrow SiO(g) + CO$$

$$SiO + 2C \leftrightarrow SiC(s) + CO$$





SILISIUM CARBIDE

1. **Silisium carbide (SiC)** is an extremely hard sharp and agressive abrasive.
2. It is also chemically very stable and hence is an appropriate material for the membrane filters used for water treatment.
3. SiC has a very high thermal stability and finds an application as the refractor material such as casting pot material.

- BLACK SiC
  Contains some free Silicon and is not as pure as
- GREEN SiC

Typical Chemical Analysis (w%)

	Black SiC	Green SiC
SiC	98,0	99,5
Silicon	0,5	<0,1
SiO_2	0,6	0,2
Carbon	0,2	0,6
Iron	0,2	<0,1
Aluminium	0,3	<0,1
Calcium	<0,1	-
Magnesium	<0,1	-

SILISIUM CARBIDE MARKET

SiC MARKET per SECTOR of ACTIVITY

•REFRACTORIES & FORGING : 690,000 MT	**60%**
•ABRASIVE & CERAMICS : 320,000 MT	**28%**
•ELECTRO –PRODUCTS : 140,000 MT	**12%**

SiC PRICE INFORMATION

1.SiCBLACK FEPA 12-220 (1815µm to 68µm)

-C&F CONTINENTAL EUROPE :

Grade 1 USD/MT :from	**1520 to 1680**
Grade 2 USD/MT :from	**1320 to 1580**

-C&F UK

Grade 1 Euro/MT :from	**1700 to 2100**
Grade 2 Euro/MT :from	**1500 to 1700**

2.SiCGREEN FEPA 12-220,over 99,5%*

-C&F CONTINENTAL EUROPE:

UK POUND/MT : from	**1840 to 2080**

SILISIUM CARBIDE MARKET

SiC MARKET TOTAL WORLD 1.000,000 to 1.150,000 MT

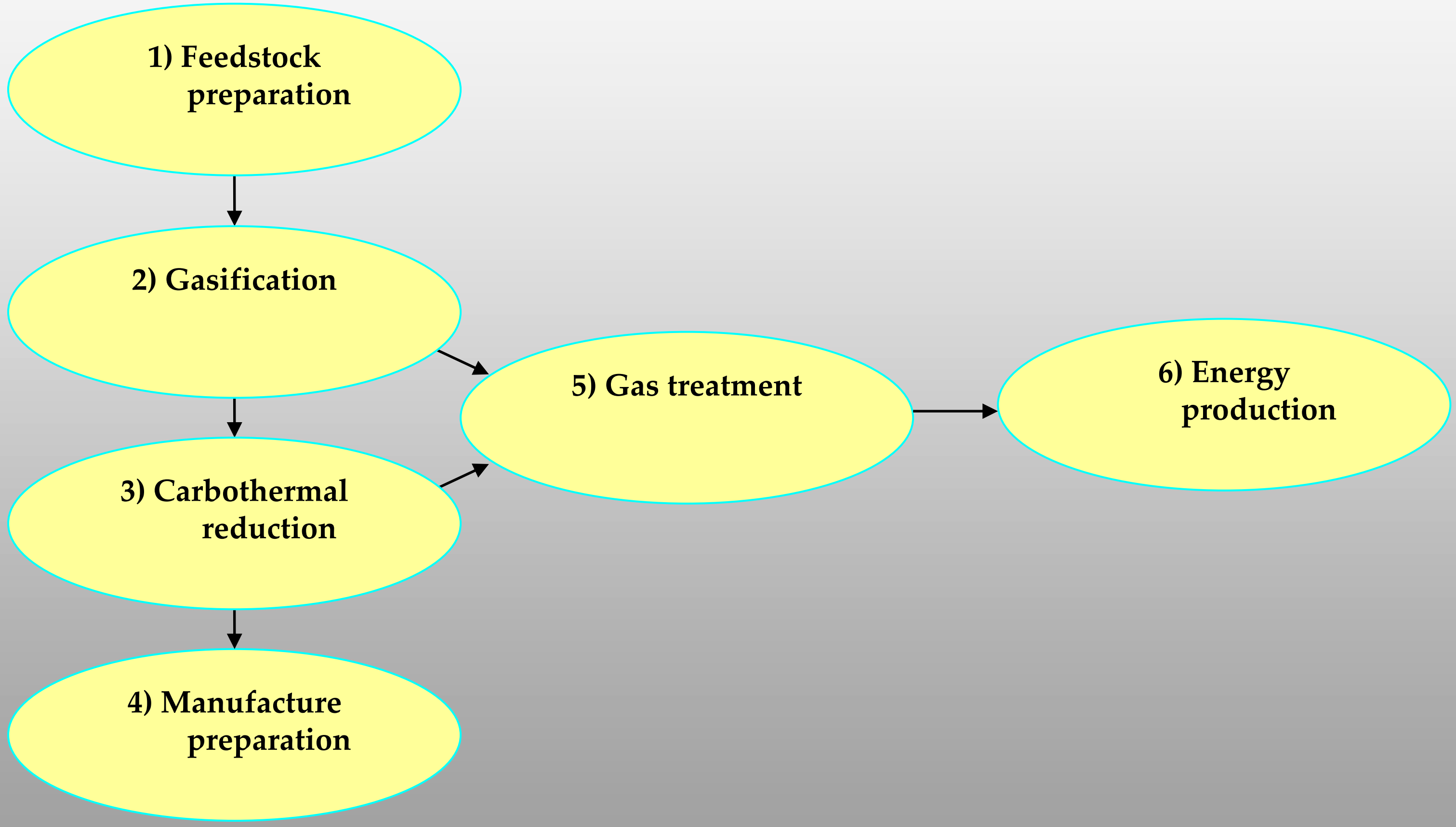
• CHINA :	+/-640,000 MT	**56%**
• AMERICAS :	+/-206,500 MT	**18%**
• EUROPE :	+/-176,000 MT	**15%**
• MIDDLE EAST :	+/-30,000 MT	**3%**
• JAPAN :	+/-27,000 MT	**2%**
• Others or Uknown :	+/-70,500 MT	**6%**

SiC IMPORTS / EXPORTS

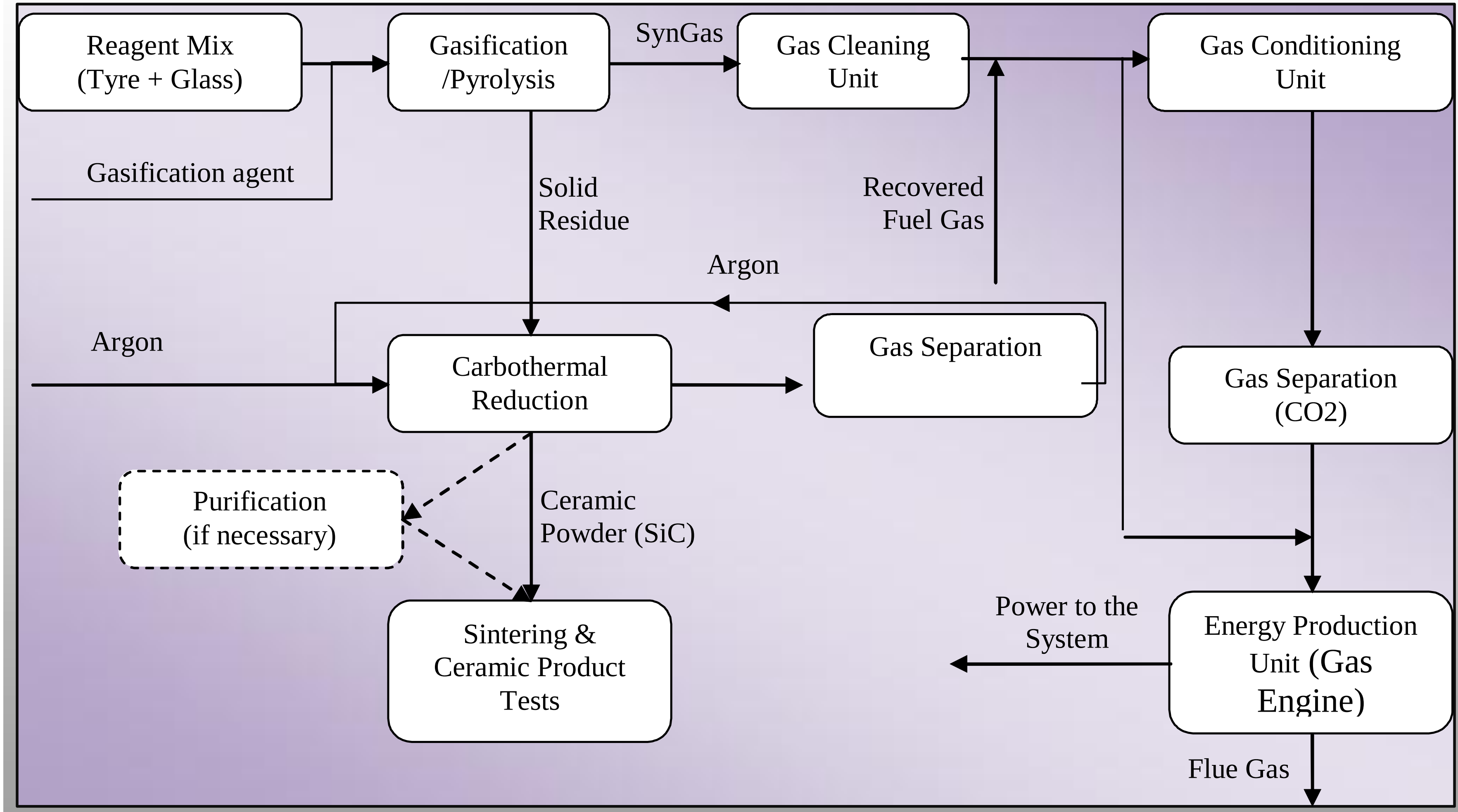
CHINA IS THE MOST IMPORTANT EXPORTER TO 50 COUNTRIES : 235,000 MT

•JAPAN :	97,000 MT	41%
•U.S.A. :	94,000 MT	40%
•SOUTH KOREA :	16,500 MT	7%
•TAIWAN :	8,500 MT	4%
•MEXICO :	4,500 MT	2%
•OTHERS :	14,500 MT	6%

PROJECT LAYOUT



PROJECT LAYOUT



PROJECT WORKPACKAGES

Workpackages	
WP0	Project Administration
WP1	Gasification and Gas Cleaning
WP2	Gas Separation
WP3	Energy Production
WP4	Carbothermal Reduction
WP5	Ceramic Product Tests
WP6	Setup and operational tests on prototypal scale
WP7	Sustainability assessment
WP8	Market analysis and Exploitation of results
WP9	Dissemination of results

TUBITAK MRC EI RESPONSIBILITIES

Within the expertise of TUBITAK MRC EI, the Institute is involved in the project as

- The work package leader of WP3-Energy Production
- The main partner in WP1-Gasification and Gas Cleaning and
- The main partner in WP6-Setup and Operational Tests on Prototypal Scale

Besides, TUBITAK MRC EI has also responsibility in work packages, namely

- WP2-Gas Separation and
- WP9-Dissemination of Results

ENERGY PRODUCTION

Objectives:

- Evaluation of the gaseous products formed during the gasification of scrap tyres for energy production
- Planning and construction of gas conditioning system
- Planning and construction of the energy production system

Table Estimated gas engine inlet fuel feed gas composition

Component	**Mole Fraction, %**
Hydrogen (H_2)	61
Methane (CH_4)	9
Carbon Monoxide (CO)	9
Carbon Dioxide (CO_2)	12
Water (H_2O)	9

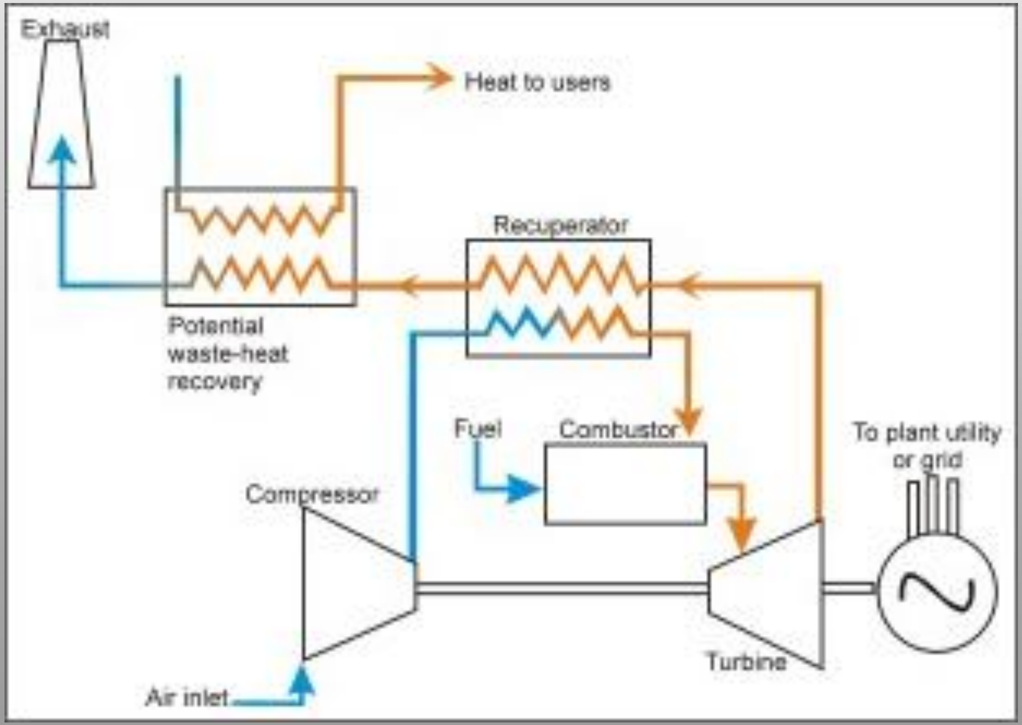
ENERGY PRODUCTION SYSTEM EVALUATION

ENERGY PRODUCTION OPTIONS

- ✓ **Micro turbine**
- ✓ **IC Engine**
- ✓ **High Temperature Fuel Cell (MCFC & SOFC)**
- ✓ **PEM Fuel Cell Cogeneration**

MICROTURBINE

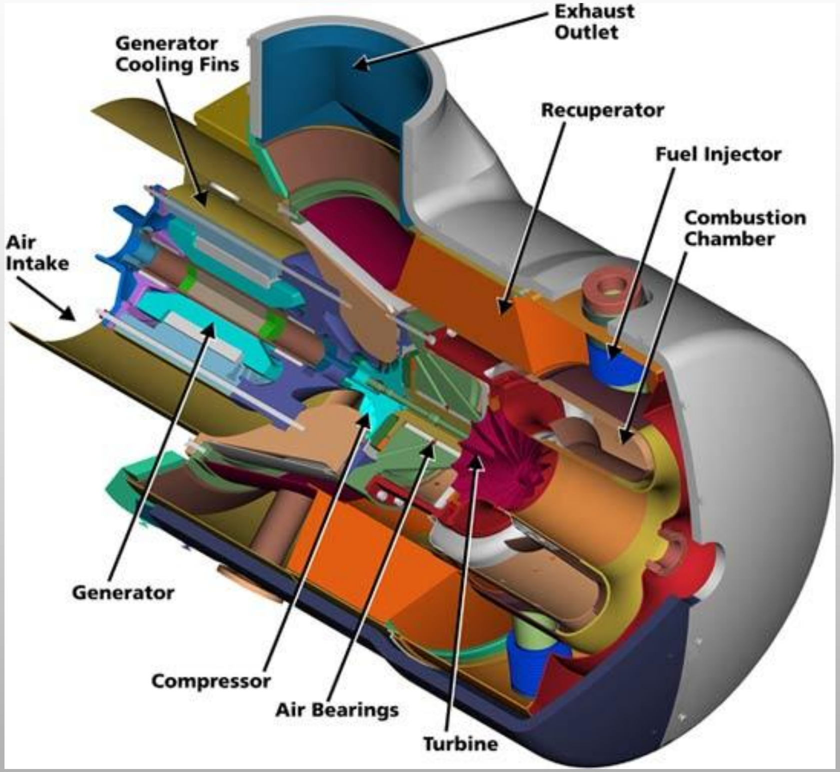
Microturbines are small single-staged combustion turbines that generate between 25 kW and 500 kW of power, which mainly used for onsite energy production. Microturbines are usually powered by natural gas, but can also be powered by biogas, hydrogen, propane or diesel.



Like fuel cells, microturbines can be paired with heat recovery systems to achieve efficiencies of up to 80%

www1.eere.energy.gov/.../microturbines.html

MICROTURBINE



www.tis.bz.it/.../image/image_view_fullscreen

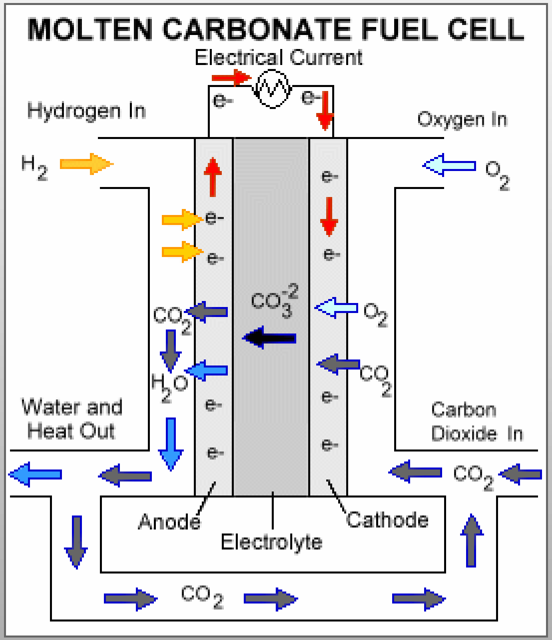
- An acceptable particle content <30 mg/Nm^3 with a particle size below 5 micron is needed.
- Deep tar elimination is required, more stiff (<50 mg/Nm3) than a gas engine.
- In addition, alkali compounds are detrimental to gas turbines, causing corrosion and deposits at the high working temperatures of turbines.
- The limits for alkali metals are;
    - Alkali metals < 0.24 mg/Nm3,
    - Ash (2-20µm: 7.5% and 0-2 µm: 92.5%) < 2 ppm,
    - Alkali (Na, K) < 0.03 ppm,
    - Calcium < 1 ppm,
    - Heavy metals (Pb, V) < 0.05 ppm.

MICROTURBINE

- The limits for sulphur containing compounds are <20 ppm.
- Finally yet importantly, halogens (HCl, HF) must be below 1 ppm.
- Standard micro turbines have approx. 50,000 hours life time (~ 6 years).
- All units have easy serviceable components, and yearly (8,000 hr) maintenance usually requires simple air and gas filter changes.
- Electrical efficiencies are in the ranges of 25%.
- NOx emmissions are expected below 10 ppmv.
- If the sensible heat of the exhaust gases is utilized high CHP efficiency is obtained.
- Microturbines cost, for commercial fuels such as natural gas or biogas, in the range of $1000/kW.
- if the hydrogen is the fuel, special and very costly hydrogen compressor is required.
- Moreover, commercial microturbines can only accept a fuel with maximum 5% H_2 content (Capstone Turbine Corporation).

FUEL CELL

A fuel cell is an electrochemical device which converts H2 or H2-rich fuels together with oxygen from air into water, along the way generating electricity and heat



- •Low temperature polymer electrolyte membrane fuel cell (PEM FC)
- •Molten carbonate fuel cell (MCFC)
- •Solid oxide fuel cell (SOFC)
- •Phosphoric acid electrolyte fuel cell (PAFC)
- •Direct methanol fuel cell (DMFC)

www1.eere.energy.gov/.../fc_types.html?m=1&

LOW TEMPERATURE FUEL CELL

- PEMFC are the best candidates for powering fuel cell vehicles as they operate at low temperature (80°C), offer short start-up time, high efficiency and good power density.

- Operational efficiency is well below the theoretical value of 65%, but it is more than twice that of typical combustion engines, with high sensitivity to operating conditions.

- Current PEMFC are less durable than combustion engines.

- Anode catalysts are sensitive to poisoning by carbon monoxide (CO) and sulphur (S). They need rather pure H_2 input from electrolysis or from reforming, with extensive clean-up.

- They also need cooling to avoid overheating.

- PEMFC may cost more than US $1800/kW (stack),

HIGH TEMPERATURE FUEL CELL

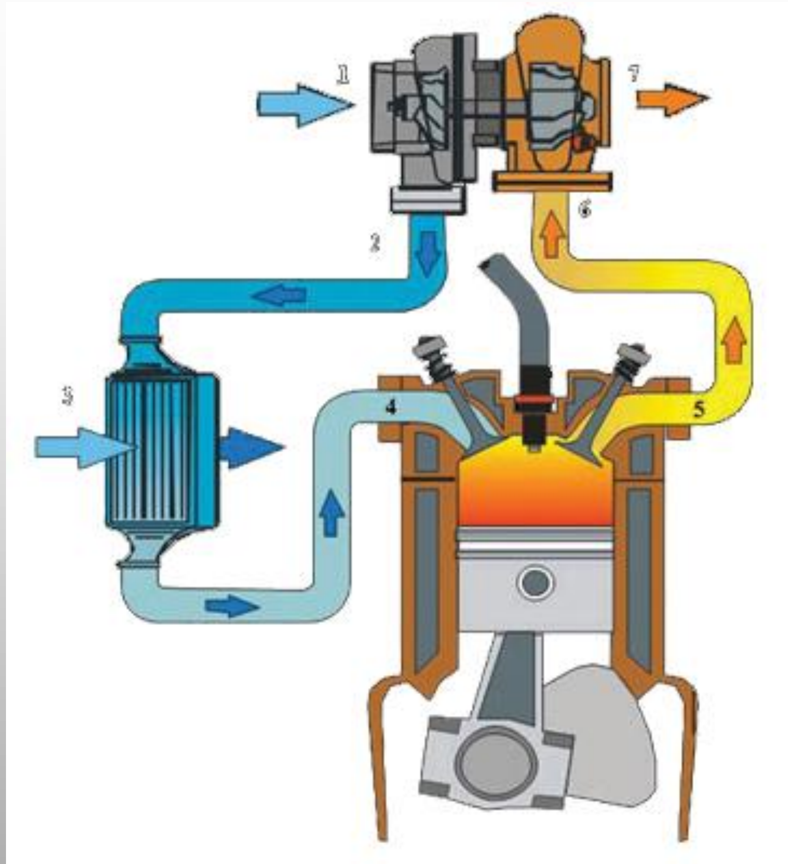
- Molten carbonate FC (MCFC) and solid oxide FC (SOFC) are the best candidates for stationary power generation.

- Both systems operate at high temperature (>650°C and 800-1000°C, respectively) and neither need costly catalysts and external reformers when running on natural gas.

- MCFC and high-temperature fuel cells like SOFC that use metallic nickel anodes. The fuel quality specification for the MCFC, for example, is for less than 10 parts per billion (ppb) of sulfur in the fuel stream going to the fuel cell stack.

- MCFC or SOFC systems cost between $12,000 and $15,000/kW (50% for stack).

GAS ENGINE



www.salvatoreaiello.com/main.shtml

•The ICE is an engine in which the combustion of a fuel (normally a fossil fuel) occurs with an oxidizer (usually air) in a combustion chamber.

• H_2 has very special properties, including

- a very high laminar flame speed,
- a high effective octane number,
- low relative density,
- wide limits of flammability,
- low ignition energies, and
- no toxicity or ozone-forming potential.

GAS ENGINE

- Depending on the high laminar flame speed H2 has also greater flashback tendency.
- High concentrations of particulates and tars can damage the engine or lead to an unacceptable level of maintenance.
- For satisfactory operation,
    - an acceptable particle content of <50 mg/Nm3
    - a particle size below 10 micron and
    - a tar content of <100 mg/Nm3 are required.
- H2-rich fuels needs special tuning of the engine components -such as injection, air to fuel ratio control etc.- implying additional costs to the system.

BEST ENERGY PRODUCTION SYSTEM FOR WASTE TIRE GASIFICATION GASEOUS FUEL STREAM

TÜBİTAK MAM

- Commercially found examples for microturbines can use fuels with lower H_2 content -a maximum of 5% H_2 content
- PEM FC option has been eliminated from the available options due to technical barriers coming from deep carbon monoxide removal and high investment and operational costs of the system. Moreover, 40-50 kWe PEM Fuel Cell is not available on the market and a tailor made manufacturing company was not at hand.
- For the 40-50 kWe energy production system, estimated cost of PEM FC stackwould be around 250 000 Euro
- The thermal management of SOFC systems is dependent on the methane/hydrogen content, and commercially available systems are currently sized for gases having significantly higher methane content (>30 vol-%) and correspondingly lower hydrogen content.
- A 50 kW SOFC system with costs higher than 2 Mio. EUR

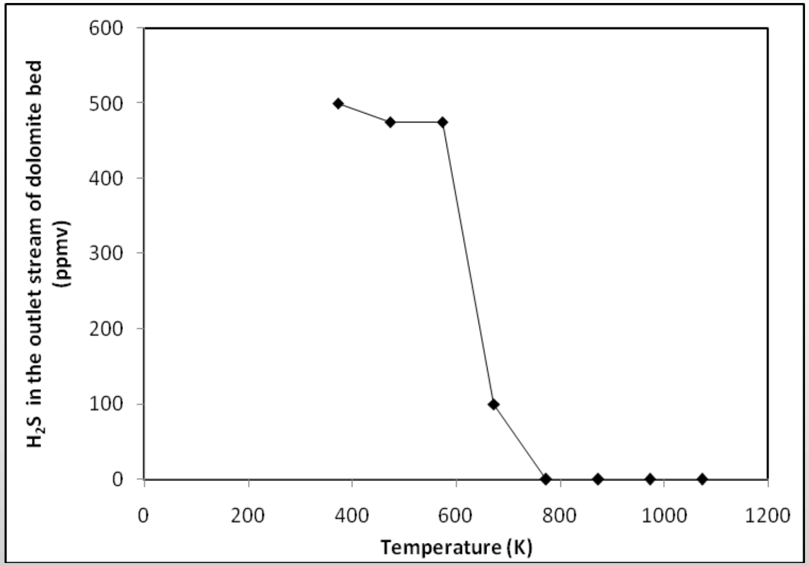
BEST ENERGY PRODUCTION SYSTEM FOR WASTE TIRE GASIFICATION GASEOUS FUEL STREAM

- Energy production from H_2-rich fuels with these systems are still on research and development state.
- Commercially available gas engine systems are custom designed for specific applications requiring
  - the addition of back flash filters and
  - venting control
- The specifications of the gas stream and also techno-economic analysis results have lead us to the <u>gas engine option</u> for the energy production unit as a final selection.

HOT GAS CLEAN-UP STUDIES

HOT GAS CLEAN-UP STUDIES

HOT GAS SULFUR REMOVAL STUDIES



Changing of H_2S concentration in the outlet stream of dolomite bed with temperature,

H_2S = 500 ppmv + N_2

GHSV = 5600 h-1,

P = 2-3 bar

The results of H_2S removal on Turkish dolomite with **tertiary** gas mixtures

Feed gas composition, %V	Contaminants, inlet (dry basis)	Outlet gas composition, %V (dry)	Contaminant, outlet
%10 CO_2, %26 H_2, %64 N_2	1280 ppmv H_2S	%7 CO_2, %15 H_2, %6 CO, %72 N_2	128 ppmv H_2S 11 ppmv COS
%10.2 CO, %11.7 H_2O, %78.2 N_2	1564 ppmv H_2S	%5.7 CO_2, %3.5 CO, %8.4 H_2, %82.4 N_2	157 ppmv H_2S 9 ppmv COS
%10 CO_2, %5 NG, %85 N_2	1700 ppmv H_2S	%9.8 CO_2, %83.6 N_2, %5.4 CH_4, %1.2 CO	70 ppmv H_2S 7 ppmv COS 0.05 ppmv EtMr
%7.9 NG, %20.9 H_2O, %71.2 N_2	1424 ppmv H_2S	%2.35 CO_2, %84.2 N_2, %10.65 CH_4, %2.8 H_2	190 ppmv H_2S 0.1 ppmv EtMr

HOT GAS SULFUR REMOVAL STUDIES

✓ Water gas shift and reverse water gas shift reactions easily occur depending upon gas composition, possibly due to the presence of iron in the dolomite composition.

✓ Sulfur removal efficiency seems to be highly dependent on sulfur concentration.

✓ When CO and CO_2 were both present in the reaction mixture, 8-10 ppmv COS formed. Also in the presence of natural gas, trace amount of ethyl mercaptane was detected in the reactor outlet gas stream.

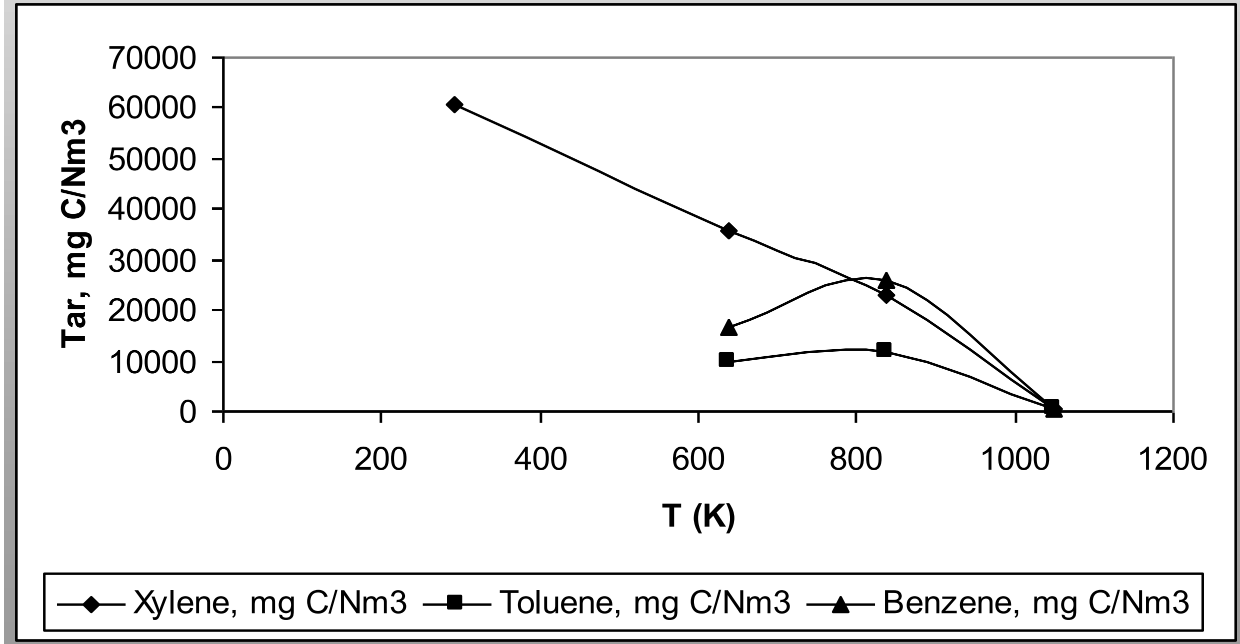
Chemical analysis of dolomite supplied from Eskişehir province of Turkey.

%Moisture	% Ignition loss	% CaO	%MgO	%SiO_2	%Fe_2O_3	%AlO_3	%MnO_4	%Na_2O
0,010	45,980	36,930	16,880	0,081	0,098	0,125	0,003	0,050

HOT GAS TAR REMOVAL STUDIES

The results of tar removal by Turkish dolomite under simulated gasifier outlet atmosphere

Feed gas composition, %V	Contaminants, inlet (dry basis)	Outlet gas composition, %V (dry)	Contaminant, outlet
% 28.5 CO, % 25.0 CO_2, % 31.4 H_2, % 3.2 CH_4, % 11.9 N_2 (dry) % 24.2 CO, % 21.3 CO_2, % 26.7 H_2, % 2.7 CH_4, % 10.1 N_2, %15 H_2O (wet)	240 ppmv H_2S 1710 mg/h Benzene 1710 mg/h Toluene 2280 mg/h Xyilene	% 35 CO, % 22.0 CO_2, % 25 H_2, % 4.0 CH_4, % 14.0 N_2	216 ppmv H_2S trace COS 3000 mg/h Benzene 1500 mg/h Toluen 250 mg/h Xylene



Changing in **tar reforming extension** via Commercial Precious Metal Catalyst **with temperature** under N_2

HOT GAS TAR REMOVAL STUDIES

✓Tar (benzene, toluene and xylene as surrogated compounds) removal activity of Turkish dolomite was shown that xylene was converted mostly into benzene and partly into toluene at 1023 K.

✓Selective steam reforming and steam dealkylation reactions were the dominant reactions in relation to steam reforming reaction over precious metal catalyst.

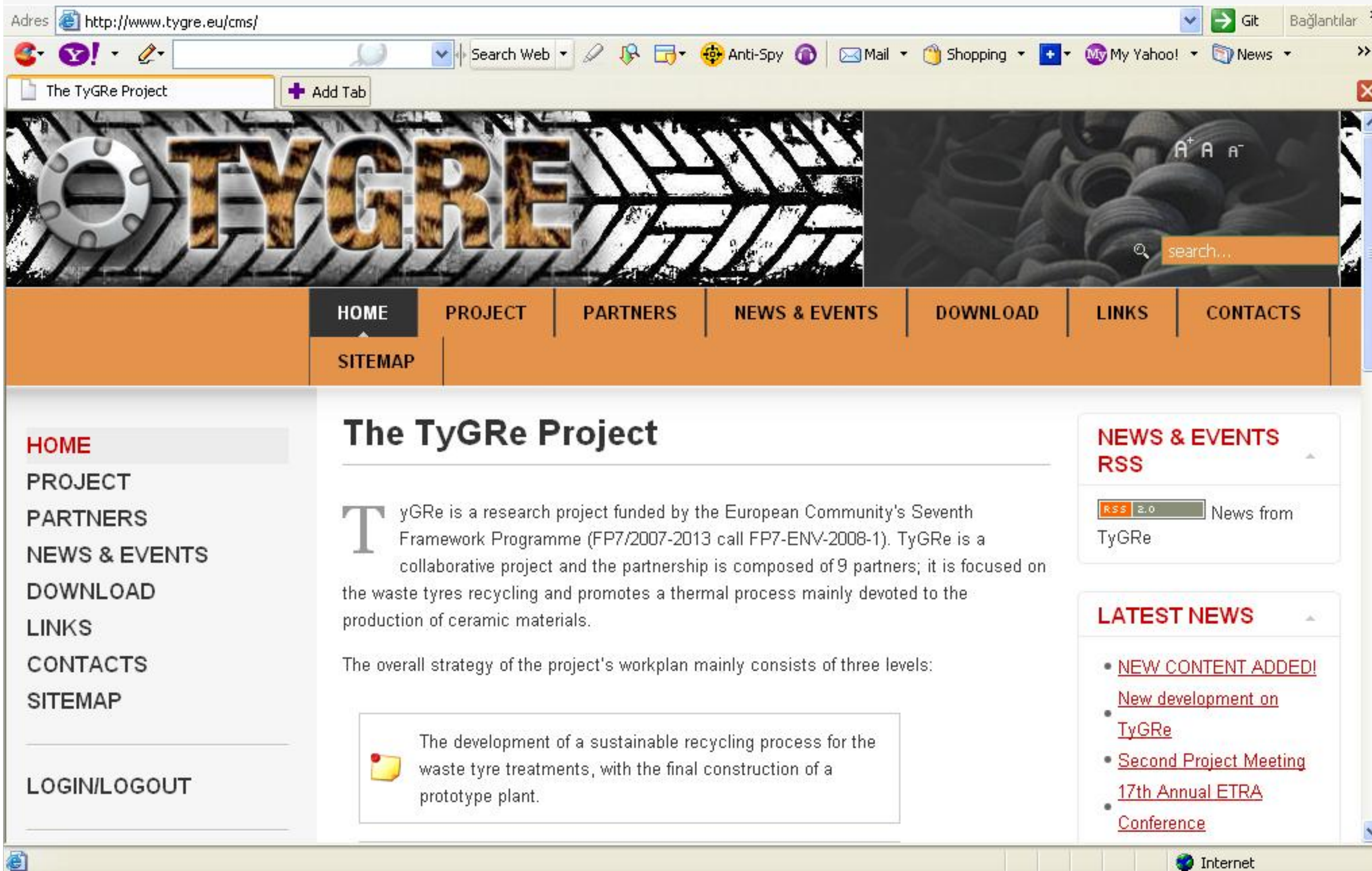
✓ The degree of dealkylation of xylene and selective steam reforming has been increased with temperature in the range of 623-1023 K.

✓Xylene conversion was seen to be dependent on inlet tar load (partial pressure of xylene). After a certain amount of inlet tar load, reaction rate becomes independent of xylene partial pressure.

the fresh (right) and used (left) catalyst

TYGRE WEB SITE

http://www.tygre.eu



THANK YOU

TUBITAK

MARMARA RESEARCH CENTER

ENERGY INSTITUE

P.O. Box.21, 41470

Gebze- KOCAELI

TURKEY

Phone: (262) 677 27 00 ; Fax: (262) 642 35 54

www.mam.gov.tr