CARBON BASED BRIQUETTES - A REVIEW

Viktor Myrvågnes

NyKoSi Seminar, Trondheim, Oct 22-23 2016

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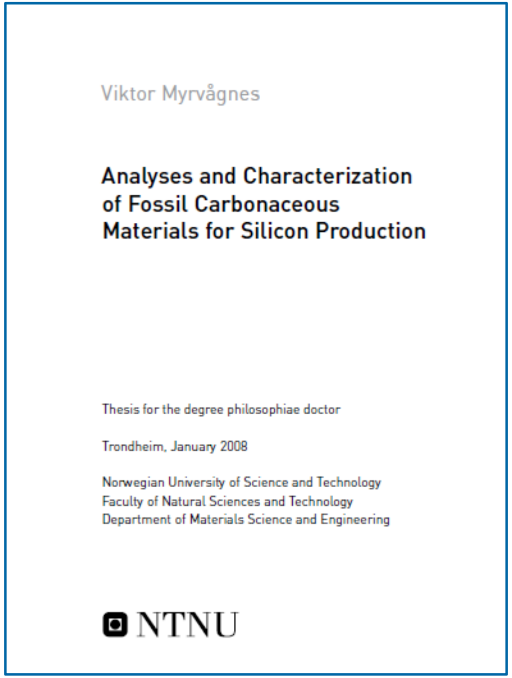
Outline

Personal interest in agglomerates


Viktor Myrvågnes

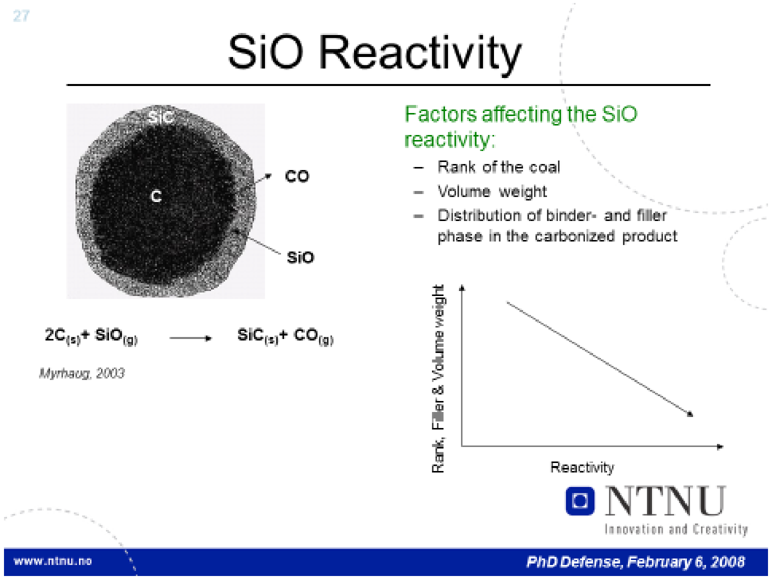
Analyses and Characterization of Fossil Carbonaceous Materials for Silicon Production

Thesis for the degree philosophiae doctor

Trondheim, January 2008

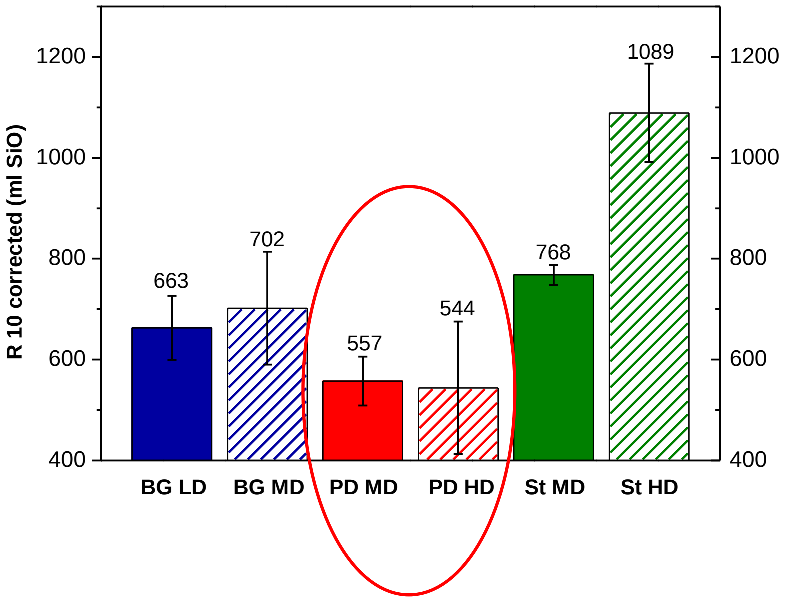
Norwegian University of Science and Technology
Faculty of Natural Sciences and Technology
Department of Materials Science and Engineering

NTNU



Results from coals with different rank and petrographical composition

SINTEF SIO REACTIVITY RESULTS (R10 CORRECTED)



DEGREE OF CONVERSION

Samples	*LD*	*MD*	*HD*
Blue Gem	80 - 85	85 - 90	
Peak Downs		95 - 100	95 - 100
Staszic		90 - 95	85 - 90

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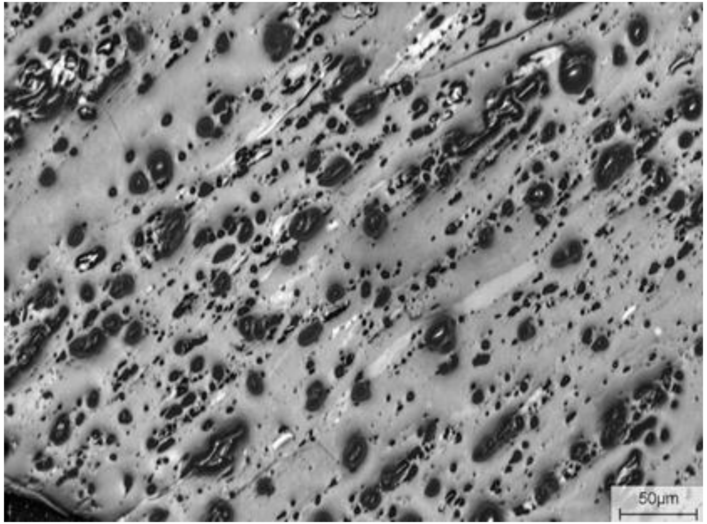
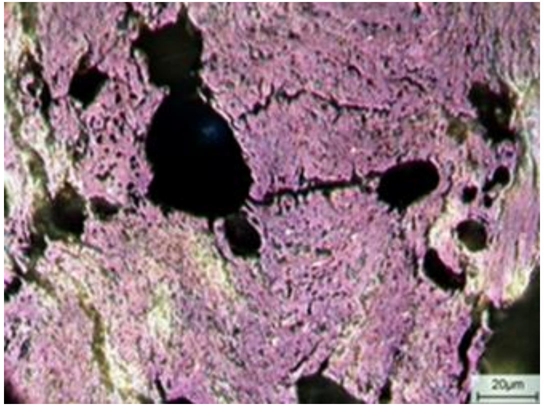
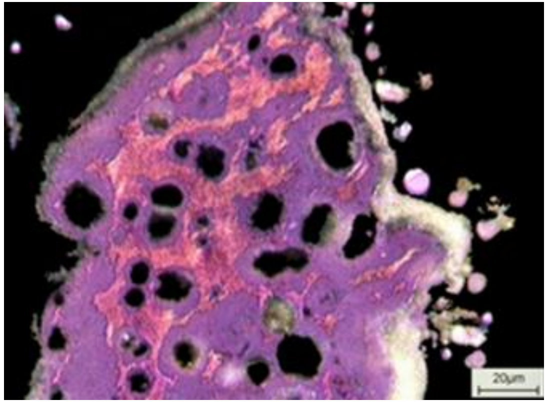
Natural agglomerates



Microphotograph of coal





Microphotographs of reacted samples

Outline

1. Introduction
2. **Briquetting with binders**
   - **Binders**
   - **Industrialized pilot plants**
   - **Laboratory Research**
3. Binderless technology
   - Industrialized technology
   - Laboratory Research
4. Briquetting technology
5. Summary

Briquetting technology
- Binders

- The binder properties:
  - Produces a strong briquette
  - Does not reduce the quality of the carbon material
  - Does not interfere with the use of the carbon
  - Is environmentally acceptable
  - Is economically viable
- The most successful binders have been:
  - Pitch (replaced by Bitumen)
  - Bitumen
  - Lignosulphonates
  - Molasses
  - Starch
  - Binder with lime
  - Resin, styrene and esters

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Ancit briquettes

SMOKELESS FUELS / HOT BRIQUETTING / SANDANCIT

- Smokeless briquettes developed as heating fuel in the 1960's by DSM
- Alsdorf plant using hot briquetting with coking coal and breeze as raw materials
- Temperature at about 500 deg C
- Post hardening step for obtaining desired strength
- Plant shut down after severe fire

- In the 80's the plant was re-started by Laborlux
- Developed the sandancit briquette
- 50% quartz sand, 50% petcoke with coking coal as binder
- Tested at Kemanord

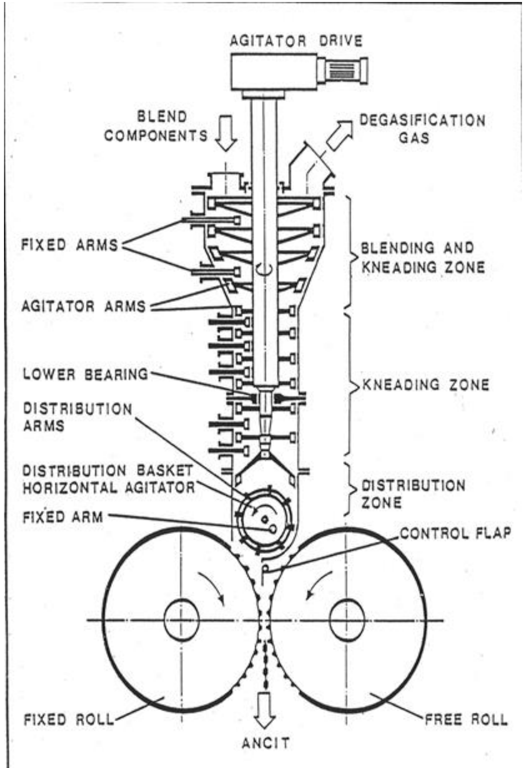

FIG. 2: FUNCTIONAL DIAGRAM OF MIXER AND ROLLER PRESS

LABORLUX ANCITFABRIK | ANCIT FORMED COKE AND FORMED BLEND COKES BY HOT BRIQUETTING | F. BECKMANN A. WAGNER

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SILGRO briquettes

AIMCOR PLANT IN ROTTERDAM

- In the 90's AIMCOR built a 100.000 tpy briquetting plant in Rotterdam
- Raw materials: green petcoke, coal, quartz sand, lime and a catalyst
- Binder: Coal tar pitch
- C/SiO_2 molar ratio: 5:1
- Green briquettes calcined in rotary kiln with sand bed at about 550 deg C
- Poor thermal and mechanical properties
- Industrial test reported high disintegration and fines generation of briquettes
- Plant shut down

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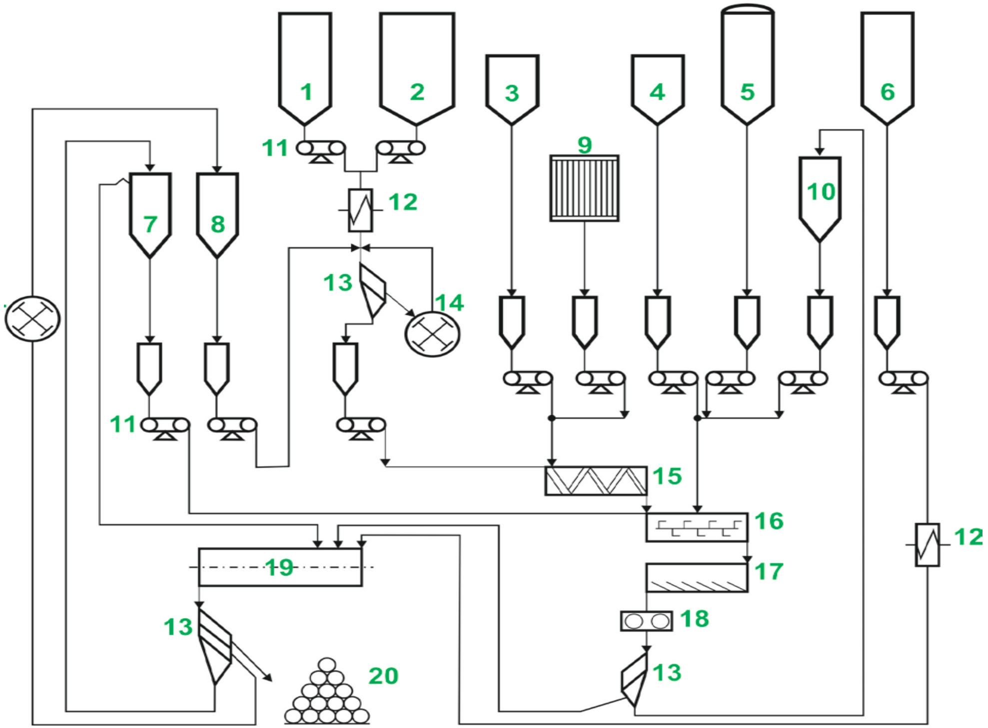
AIMCOR Silgro plant
- Principle



1-6:	Raw material bins
7-10:	Recycle
11:	Scales
12:	Dryer
13:	Screen
14:	Crusher
15:	Pre-heater
16:	Mixer
17:	Cooler
18:	Roller press
19:	Rotary kiln
20:	Briquettes

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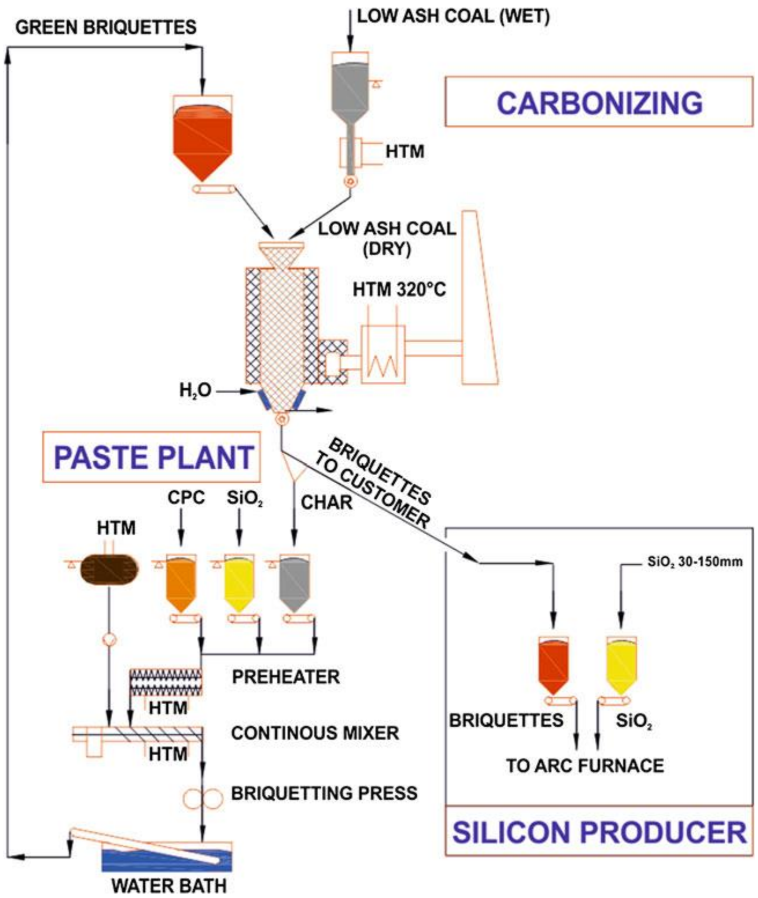
Carbosil

DEVELOPED BY R&D CARBON

- High purity Carbosil briquettes developed for direct UMG-Si production in SAF
- Binder: HT coal tar pitch
- Molar ratio C/SiO_2: 5:1
- Co-carbonization process:
  - Green granular carbon and green briquettes
  - 750 deg C
  - Vertical retort
- Reference: JOM (2013) 65:1744-1748



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Carbosil

FURTHER INFORMATION

- Granular carbon materials co-carbonized with green briquettes in a vertical retort at final temperature at about 750 deg C
- Carbon dry aggregate prepared by crushing and screening in a continuous pilot roller crusher and multideck screening machines
- Dry aggregate is mixed and pre-heated before mixing in a high intensive propeller mixer
- Paste is cooled by water addition to the right temperature before briquetting
- Green briquettes co-carbonized in vertical retort in order to obtain desired strength

Dry aggregate preparation

Intensive mixing

Briquetting press

Vertical retort

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Carbosil properties

VS ANCIT AND SILGRO

- Similar molar ratios of C:SiO_2 (5:1)
- Highest density of the Carbosil briquettes
- Highest strength (load strength)
  - Due to intimate mixing of dry aggregate and size control before compression
- Carbosil briquettes are more suitable for UMG-Si production due to lower ratio of non-SiO_2 ash components
- Silgro and Sandancit have similar values of loss and dust formation in CO_2. Both superior to the Silgro briquettes

Table I. Comparison of Carbosil with Previous Industrial Briquettes (Ancit and Silgro)

Apparent density	kg/dm^3	1.49	1.35	1.52
Load strength	kg	120	80	140
Loss in CO_2	%	14	18	13
Dust in CO_2	%	11	54	9
Ratio loss/dust	–	1.2	0.3	1.4
Volatiles	%	4	6	3
Non SiO_2 ash	%	3	2	0.2

FeSi agglomerates

PATENTED BY OLA RAANESS

- US patent 1998
- Raw Materials
  - Swelling coal (FSI=8-9)
    - Size: < 3 mm
    - Moisture: < 3 wt%
  - Iron slags
    - Size: < 106 µm
- Carbon to Fe ratio (mass): 0,2-1:1,5 (prefferred 1,2:1)
- No binders in the laboratory test
- Possible binders: CTP, bitumen

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FeSi agglomerates patented by Ola Raaness

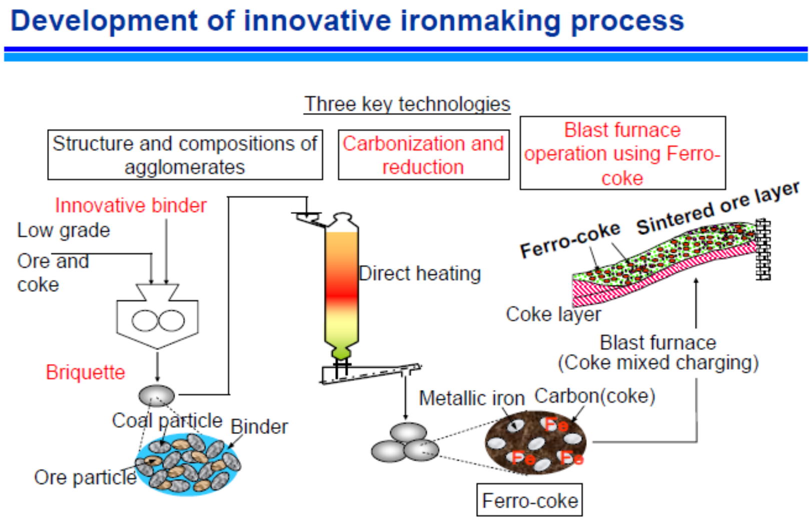
LABORATORY TESTS

- Coal to slag weight ratio: 0,8-1,5:1
- Briquetting:
  - Cool pressing
  - Load: 10-20 tonnes
  - Cylindrical briquettes with d = 30 mm
  - Length of green briquettes = 10-15 mm
- Sintering
  - 400-500 deg C for 30 min
  - Alsint crucible with lid in air

PILOT BRIQUETTING PLANT

- Raw materials:
  - Coal size: < 2 mm
  - CTP as binder (6-7 wt%)
- Coal to slag weight ratio: 1,8:1
- Continous roller press
- Sintering:
  - 400 deg C for 10 min
  - Air atmosphere
- Briquettes
  - Pillow shaped
  - Dimension 35x35x20 mm

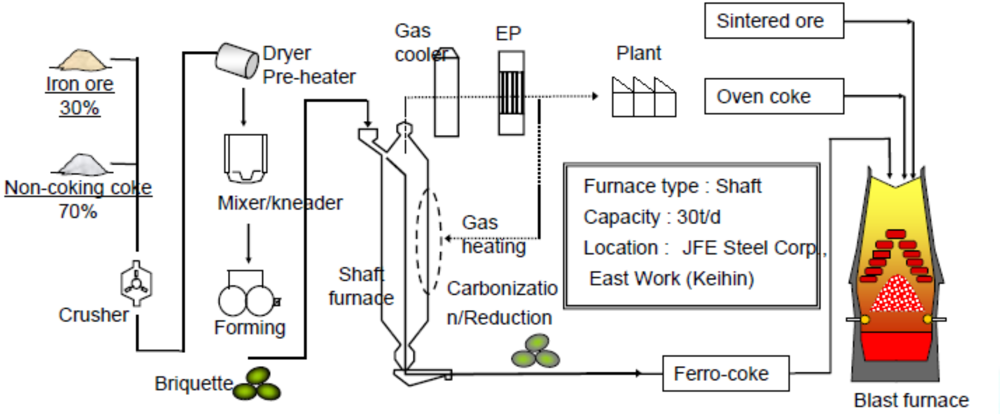
NEDO – Development of Ferrocoke for use in blast furnaces
- JFE Steel, Nippon Steel and Kobe Steel



- Raw Materials:
  - Weakly caking and non-caking coals
  - Ore
  - Innovative binder from the Hyper Coal process
- Coal / ore ratio: 7:3
- Binder: 5-9 wt%
- Briquetting temperature: 100 – 120 deg C
- Size: 30x25x15 mm
- Calcination in shaft furnace
- Coking temperature: 800 – 1000 deg C
- Briquettes tested at blast furnace (No. 6) at Chiba works

JFE, Nippon Steel, Kobe Steel

Process flow of the Ferrocoke plant



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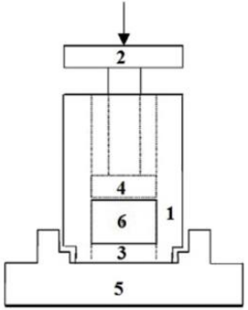
Water resistant briquettes from Turkish lignite

- Coal size: < 3 mm
- Binder: Co-polymer binder Mowilith-VDM
- Briquetting: Hydraulic press
- Pressure: 30 – 60 MPa
- Briquette size: 30 mm diameter
- Addition of molasses increased strength
- Lime did not show any positive influence on the shatter index

Piston Press

Press and pressing molds

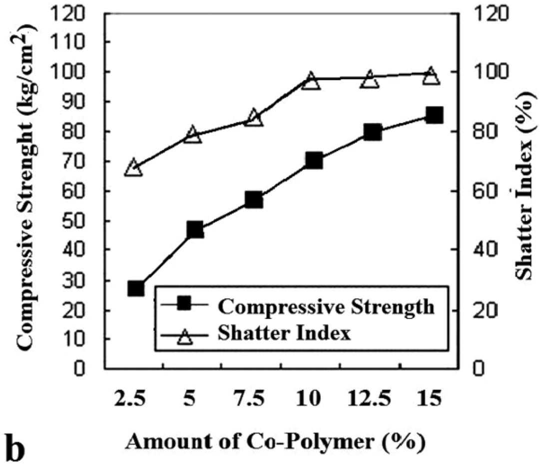


1, steel mold
2, steel pressing piston
3, steel disc bottom
4, steel disc top
5, steel down plate
6, sample position

Briquettes form

Water resistant briquettes from Turkish lignite
- Results

- Compressive strength correlated with increased ratio of bituminous coal due to the higher inherent compressibility of bituminous coal
- Strength increased with addition of binder



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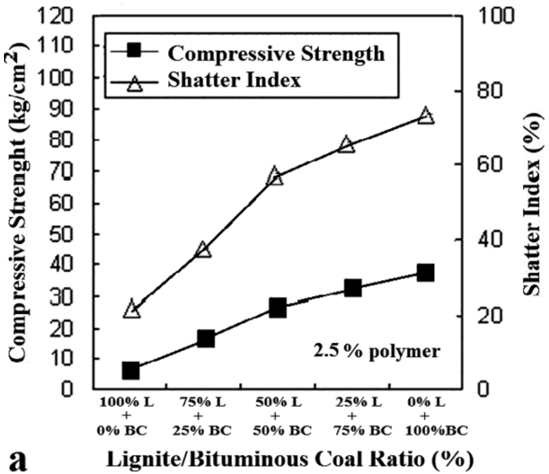

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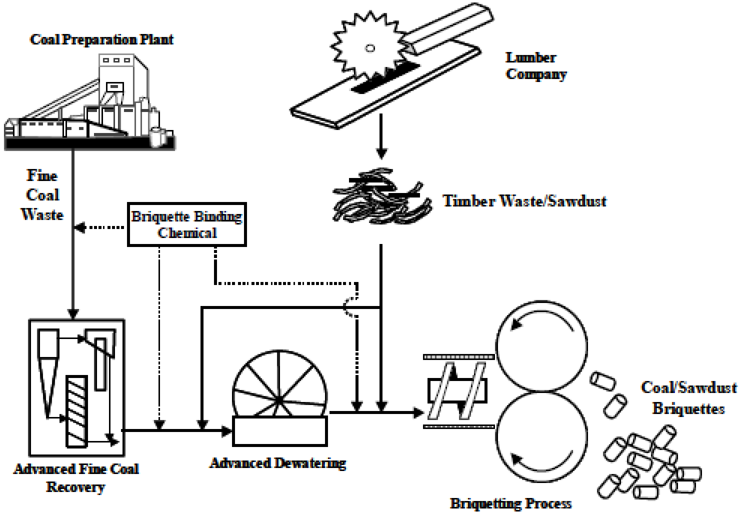
Briquetting of coal fines and saw dust

- Centre for Applied Energy Research, University of Kentucky

- Business Case:



- Briquetting process:
  - 90 wt% coal fines, 10 wt% saw dust
  - Diameter: 25,4 mm
  - Load: 4000 lbf
  - Temperature: 22 deg C
- Tests:
  - Compressive strength
  - Water resistance
  - Shatter resistance
  - Attrition index

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Briquetting of coal fines and saw dust
- Information

- Equivalent – cost basis
  - Cost 8 USD/nt as the binder application rate
- More than 10 binders evaluated
- Evaluation of binders
  - Best:
    - Guar gum
    - Wheat starch
    - Reax+2 wt% lime
  - Other potentials
    - Black strap molasses
    - Paper sludge
    - Tall oil emulsions
    - Molasses
    - Coal tar

- Coal samples:
  - Bituminous coal rank
  - Coal fines from JRC and Cooke and Sons Mining
  - 20-25 wt% moisture
- Saw dust
  - Mix of three species (or pure species)
    - White Oak
    - Red Oak
    - Poplar
  - Size: < 6,3 mm

Briquetting of coal fines and saw dust

- Results (Compressive strength, 90wt% coal and 10wt% saw dust)

Binder ID	Binder Wt %	Green Strength	1-day Strength	7-day Strength
Peridur 300	0.4	34.3	35.7	180.4
Western Bentonite	6.7	34.5	35.1	70.9
Wheat Flour, Wal-Mart	3.4	39.2	37.8	126.1
Spring Wheat Flour	7.2	42.6	42.5	161.3
Lavabond	6.7	30.5	40.0	71.0
Corn Starch	2.9	39.0	51.0	121.2
Black Strap Molasses	6.4	33.1	37.0	49.9
Coal Loading Tar	5.0	43.4	39.9	73.6
Paper Sludge	17.8	41.0	29.2	33.8
Lime	8.0	45.6	32.6	67.1
RS-2	4.8	32.8	22.6	23.2
Sodium Silicate	8.0	31.3	68.9	73.6
Polybond 300G	6.2	30.2	33.7	55.4
Polybond	9.4	25.7	34.1	45.9
Guar Gum	1.0	43.7	70.4	142.9
Bleached Softwood pulp	1.5	54.6	35.8	34.4
Brewex	17.8	41.4	40.7	73.9
Wheat starch 7	1.0	35.6	37.6	93.2
Wheat starch 6	2.9	45.2	53.6	141.3
Reax	4.8	31.5	34.5	61.1
Cola Syrup	12.3	33.0	28.5	
Asphalt-SS	4.8	39.2	31.1	
Asphalt-MS	4.8	29.6	26.9	
No binder (Control)	0.0	30.9	19.3	

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Briquetting of coal fines and saw dust
- Results (Comparison of physical properties)

Binder ID	Binder Wt %	green Strength	1-day Strength	7-day Strength	Drop Test #drops	H20 resist (lb_f CS)	Attrition Index
Black Strap Molasses*	6.70	**91.7**	**102.4**	**174.9**	17.8	disintegrated	55.5
Hi-Gluten Wheat Flour	2.90	**64.7**	78.4	**>200**	**46.8**	24.1	**67.5**
Guar Gum	1.00	**63.6**	86.1	**>200**	**51.3**	41.7	**81.1**
Hi-Starch Wheat Flour	2.89	51.3	61.7	**>200**	27.3	17.8	56.8
Corn Starch	2.9	50.4	66.2	**169.8**	24.8	36.8	46.0
Paper Sludge*	17.90	**78.4**	83.7	135.8	4.3	85.0	36.0
Wheat starch 6	2.90	**58.1**	N/A	**>200**			**71.7**
Control w/ lime only	2.00	**57.6**	N/A	45.5	1.0	35.9	31.1
Tall Oil Emulsion*	5.3	45.9	38.0	64.4	2.8	42.5	34.1
Molasses*	5.7	55.9	71.4	**151.5**	9.0	disintegrated	55.2
Reax*	4.3	43.7	**89.0**	**>220**	**>100**	disintegrated	**91.1**
Reax & ASPHALT*	2.5&1.2	59.6	87.5	**195.2**	28.0	58.2	50.4

Outline

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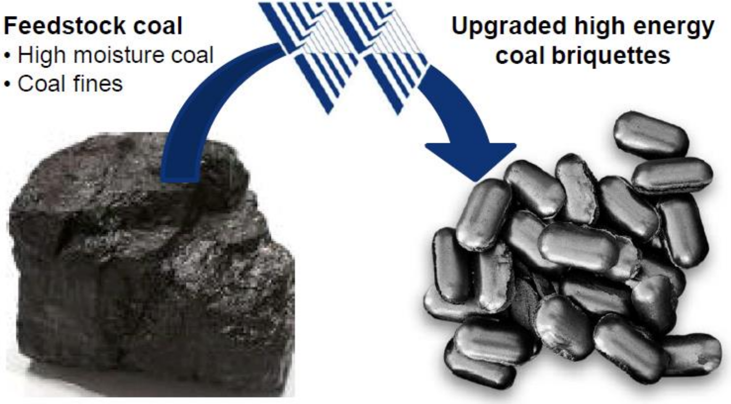
2. Briquetting with binders
   - Binders
   - Industrialized pilot plants
   - Laboratory Research
3. **Binderless technology**
   - **Industrialized technology**
   - **Laboratory Research**
4. Briquetting technology
5. Summary

White Energy Process (BCB) developed by CSIRO

- Binderless Coal Briquetting (BCB) Process using dehydration and compaction
- Upgrading of brown coals
- Establishment of 1 million tonnes per year plant in Kalimantan



Sub-bituminous coal example

Indonesia
Approx. 4,400 Kcals/kg GAR → Approx. 6,100 Kcals/kg GAR

PRB Coal
Approx. 8,400 Btu/lb GAR → Approx. 11,350 Btu/lb GAR

* GAR = Gross As Received

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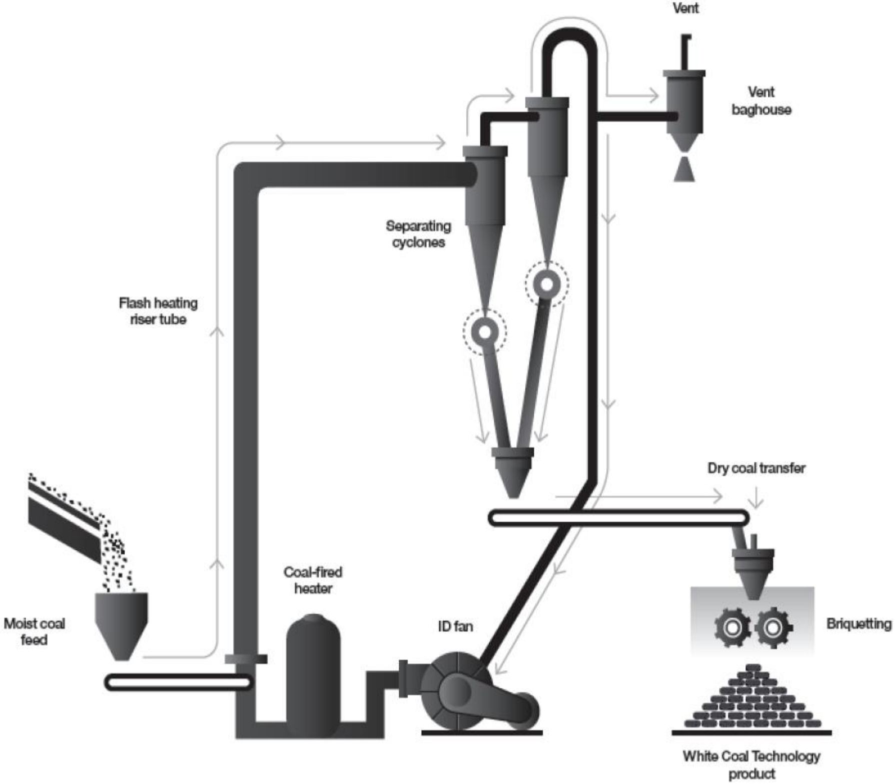
White Energy Process (BCB) developed by CSIRO

- Coal crushed to < 3mm
- Flash dried to moisture level 7-8 wt%
- Compacted and briquetted, creating tight bonds between coal particles and eliminating nearly all voids
- Patented briquetting machines by Komarek
- Briquettes cooled to enable handling and storage
- Resulting in a higher density, higher energy briquette with low permeability and reduces propensity towards spontaneous combustion



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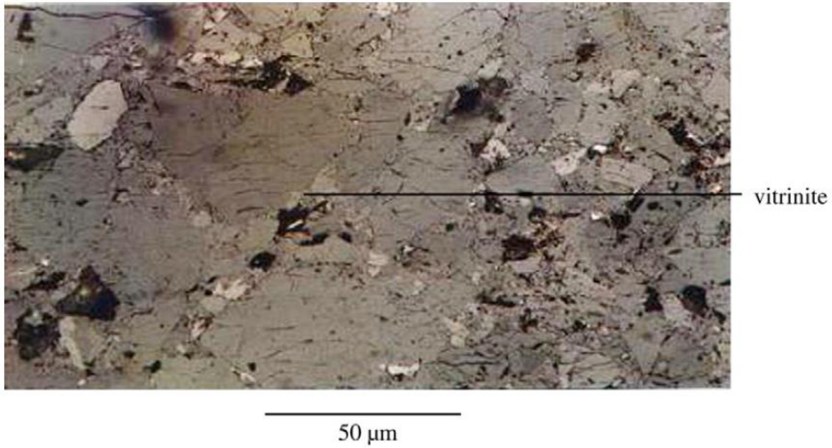
South-African prime coking and blend coking coals

- Coking coals with high proportions of vitrininte
- Bonding mainly created by deformation and consolidation of vitrinite
- Weathering (oxidation) has an adverse effect on the suitability of coal for binderless briquetting
- Coal size: < 2 mm
- Ash: 10 wt%



Petrographic properties of Samples A and B coal

Colliery	% Vitrinite	% Liptinite	% Reactive inertinite	% Inert inertinite	% Total inertinite	% Reactives	$\bar{R}_r$%	Rank
Sample A	91	1	1	7	8	93	1.26	Medium rank B
Sample B	86	6	3	5	8	95	0.72	Medium rank C

Note: Maceral analysis — percentage by volume, mineral matter-free basis (mmf).

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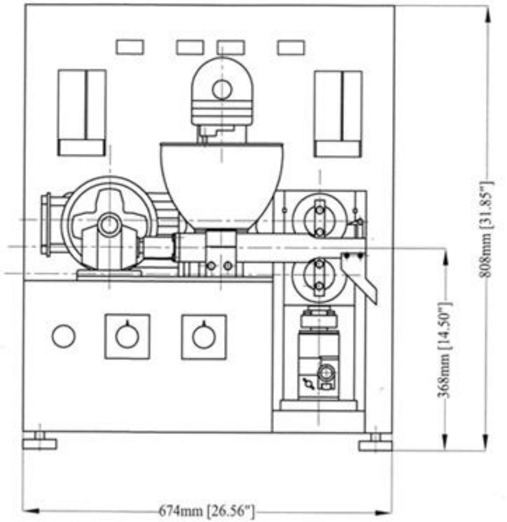
South-African coking coals
- Process and results

- Pillow shaped briquettes: 40 x 19 x 13 mm
- Maximum pressure: 17 MPa
- Komarek B-100A roll type briquetting machine



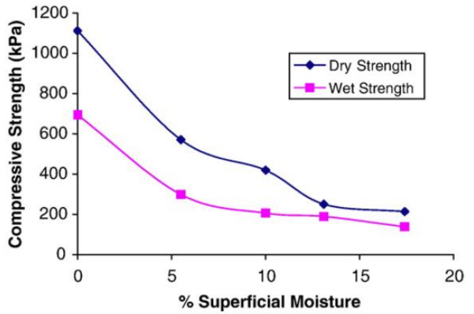


Fig. 2. Compressive strength of briquettes against superficial moisture content of the Sample A.

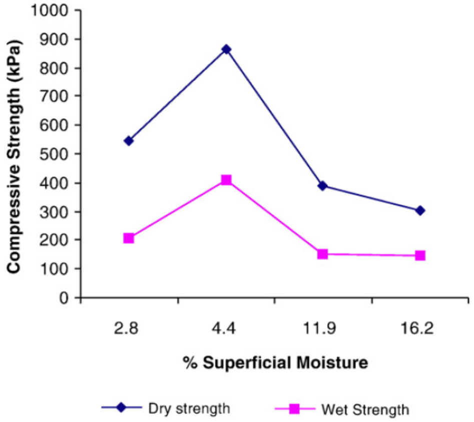


Fig. 4. Plot of the mean dry and wet compressive strengths of briquettes against feed moisture content of Sample B.

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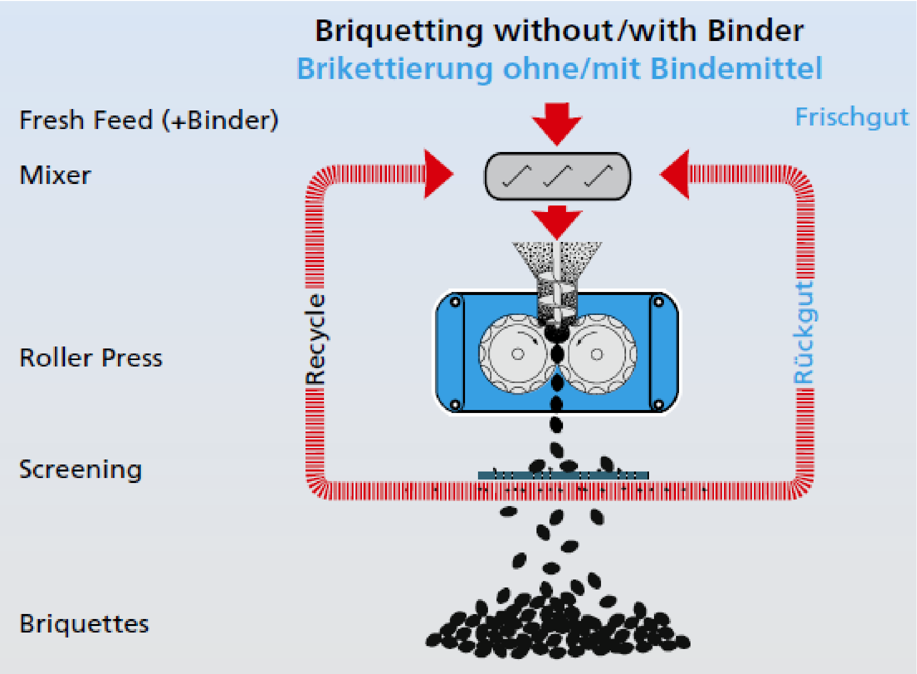
5. Summary

Briquetting Technology
- Generalized Flowsheet

- Size preparation: Correct size distribution
  - Coal size: < 2 mm
- Moisture control
  - Optimal moisture for optimal properties
- Mixing coal and binder
- Briquetting process
- Condition the mixture if needeed
- Post formation treatment:
  - Heating, sintering
  - Cooling



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Summary

Project name or inventor	Main application	Binder	SiO_2/Fe_3O_4	Carbon RM	Sintering	Test scale	Properties evaluated	Remark
Carbosil	High pure Si production	Coal pitch	$C:SiO_2=1(W)$	Char, petcoke	750 °C	Pilot	Load strength, Apparent density, Thermal stability, CO_2 reactivity	HMS on use of pitch
Silgro	Si production	Coal pitch	$C:SiO_2=1(W)$	Petcoke, Coking coal	550 °C	Full size plant	Load strength, Apparent density, Thermal and mechanical stability	HMS on use of pitch, Thermal stability low, Loss in fines
Fesil agglomerates by Raaness	Fesil production	Coal pitch	$C:Fe_3O_4=1,8(W)$	Swelling coal, FSI=8-9	400 °C	Pilot	Thermal and mechanical stability, SiO reactivity	HMS on use of pitch
Water-resistant briquettes from Turkish lignite	Power plant	Copolymer Mowilith-VDM + Molasses	No	Lignite and bituminous	No	Laboratory	Compressive strength, Shatter index, Weathering test	Binder cost, Thermal stability unknown
Coal fines and sawdust	Power plant	Guar gum, Wheat starch, Reax + lime	No	Bituminous coal and sawdust (10%)	No	Laboratory	Compressive strength, Shatter index, Water resistance, Attrition index	Binder cost $8/ton, Thermal stability unknown
White Energy Process	Thermal coal, Metallurgical coal fines	No	No	Low ranker coal, Sub-bituminous coal, Lignite	No	1 milion tonne per annum	Mechanical stability, Thermal values	Thermal stability unknown
South African coking coal	Power plant	No	No	Prime coking and blend coking coals	No	Laboratory	Compressive strength, Water resistance (wet compressive strenth)	Thermal stability unknown

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ADVANCED MATERIALS
SHAPING THE FUTURE