

GEN3 Validation Report

Water Flow Calorimetry, Experimental Runs and Validation Testing for BlackLight Power Inc.

Performed at BlackLight

August 2009

GEN3 Validation Report

1. Goal and scope of the work

The main goal of this work was to validate the experiments of BlackLight Power on heat generation from certain hydrogen-containing solid compositions.

The scope of the work comprised participation of GEN3 expert in the whole experimental work on measuring heat generation from two chemical systems: KH+Mg+TiC+MnI₂ and KH+Mg+TiC+EuBr₂, including preparation and analyses of starting chemicals, calibration of the calorimeter, run thermal experiments, and analysis of solid and gas phases after the thermal run.

2. Preparations for the experiments

Preparations for the experiments comprised the stages of chemical preparation and calibration of the calorimeter.

2.1 Chemical Preparation

Titanium carbide, TiC, magnesium metal powder, Mg (99.8%), potassium hydride, KH (30-35% wt% in mineral oil) and europium bromide, EuBr₂ (99.99%), were all supplied by Alfa Aesar while manganese iodide, MnI₂ (98%) was purchased from Strem Chemicals, and anhydrous hexane (99%) was supplied by Sigma Aldrich. Quality and specification of the chemicals were confirmed by the manufacturer's labels on their containers (Table 1).

Table 1. Specification of starting chemicals.

Component	Purity	Supplier	Formula
Titanium carbide	n/a	Alfa Aesar	TiC
Magnesium metal	99.80%	Alfa Aesar	Mg
Potassium hydride	n/a	Alfa Aesar	KH
Manganese iodide	98%	Strem Chemicals	MnI ₂
Anhydrous hexane	≥99%	Sigma Aldrich	CH ₃ (CH ₂) ₄ CH ₃
Europium bromide	99.99%	Alfa Aesar	EuBr ₂

In preparation for the reaction, titanium carbide was first dried in a flask under vacuum of approximately 50 mTorr at 200 °C for 24 hours and then transferred to the glove box. The potassium hydride was washed with anhydrous hexane five times after decanting the mineral oil. The KH was further dried in the anti-chamber of the glove box for 4 hours to remove residual hexane and other organic residues, and later transferred into a sealed container inside the glove box.

Temperature programmed desorption (TPD) studies were done on the starting materials, europium bromide, manganese iodide and titanium carbide to quantify any condensable gases (Table 2). A certain amount of sample was loaded into a TPD cell under inert atmosphere, the cell was further placed inside a thermal heater and connected to a gas line (including stainless steel tubing and reservoir). Before heating, the sample and gas line were evacuated to $\sim 10^{-5}$ Torr vacuum. The cell was then heated slowly to roughly 500 degrees C. The evolved gas was expanded into stainless steel tubing/reservoir of known volume. To trap condensable gas, a reservoir attached to the gas line was submerged in a liquid nitrogen dewar. The condensable water vapor or other gas(es) from the thermal desorption is trapped and immobilized in the cold trap. After evacuating the noncondensable gas(es), the cold trap was removed to allow the reservoir to warm to room temperature. The condensed gas will evaporate as the temperature increases. In the experiment, cell temperature, room temperature, and gas pressure were monitored and acquired by LabView program. With the measured P, V and T, the quantity of gas can be obtained according to the ideal gas law.

Table 2. Amount of condensable gas from TPD of starting chemicals.

Sample	RT (°C)	P (Torr)	Volume (mL)	Weight (g)	N (mole)	N (mole/g)
MnI ₂	24.5	1.06	314.3	0.49	1.795E-05	3.663E-05
EuBr ₂	24.8	5.13	314.3	0.535	8.677E-05	1.622E-04
TiC	24.3	2.15	314.3	0.53	3.643E-05	6.873E-05

Water-Flow, Batch Calorimetry. A schematic of the cylindrical stainless steel reactor of approximately 130.3 cm³ volume (1.5" inside diameter (ID), 4.5" length, and 0.2" wall thickness) is shown in Figure 1. The water flow calorimeter comprising a vacuum chamber containing each cell and an external water coolant coil that collected 99+% of the energy released in the cell to achieve an error $< \pm 1\%$ is shown in Figure 2. The energy recovery was determined by integrating the total output power P_T over time. The power was given by

$$P_T = \dot{m}C_p\Delta T \quad (1)$$

where \dot{m} was the mass flow rate, C_p was the specific heat of water, and ΔT was the absolute change in temperature between the inlet and outlet. The reaction was initiated by applying precision power to external resistive heaters. Specially, 200 W of power was supplied to the heater for 130.3 cm³ cell. During this heating period, the reagents reached a temperature threshold wherein the onset of the reaction was typically confirmed by a rapid rise in cell temperature. Once the cell temperature reached about 400-500 °C the input power was set to zero. To increase the rate of heat transfer to the coolant, the chamber was re-pressurized with above atmospheric pressure of helium, and the maximum change in water temperature (outlet minus inlet) was approximately 1.2 °C. The assembly was allowed to fully reach equilibrium over a 24-hour period as confirmed by the observation of full equilibrium in the flow thermistors.

In each test, the energy input and energy output were calculated by integration of the corresponding power. The thermal energy in the coolant flow in each time increment was calculated using Eq. (1) by multiplying volume flow rate of water by the water density at 19 °C (0.998 kg/liter), the specific heat of water (4.181 kJ/kg °C), the corrected temperature difference, and the time interval. Values were summed over the entire experiment to obtain the total energy output. The total energy from the cell E_T must equal the energy input E_{in} and any net energy E_{net} . Thus, the net energy was given by

$$E_{net} = E_T - E_{in} \quad (2)$$

From the energy balance, any excess heat E_{ex} was determined relative to the maximum theoretical E_{mt} by

$$E_{ex} = E_{net} - E_{mt} \quad (3)$$

Figure 1. Schematic of the reaction cell and the cross sectional view of the water flow calorimeter used to measure the energy balances. The components were: 1—inlet and outlet thermistors; 2—high-temperature valve; 3—ceramic fiber heater; 4—copper water-coolant coil; 5—reactor; 6—insulation; 7—cell thermocouple, and 8—water flow chamber.

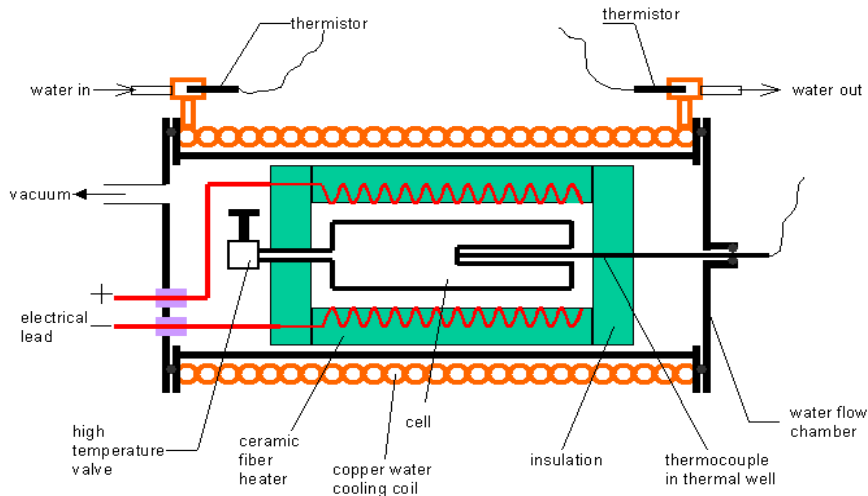
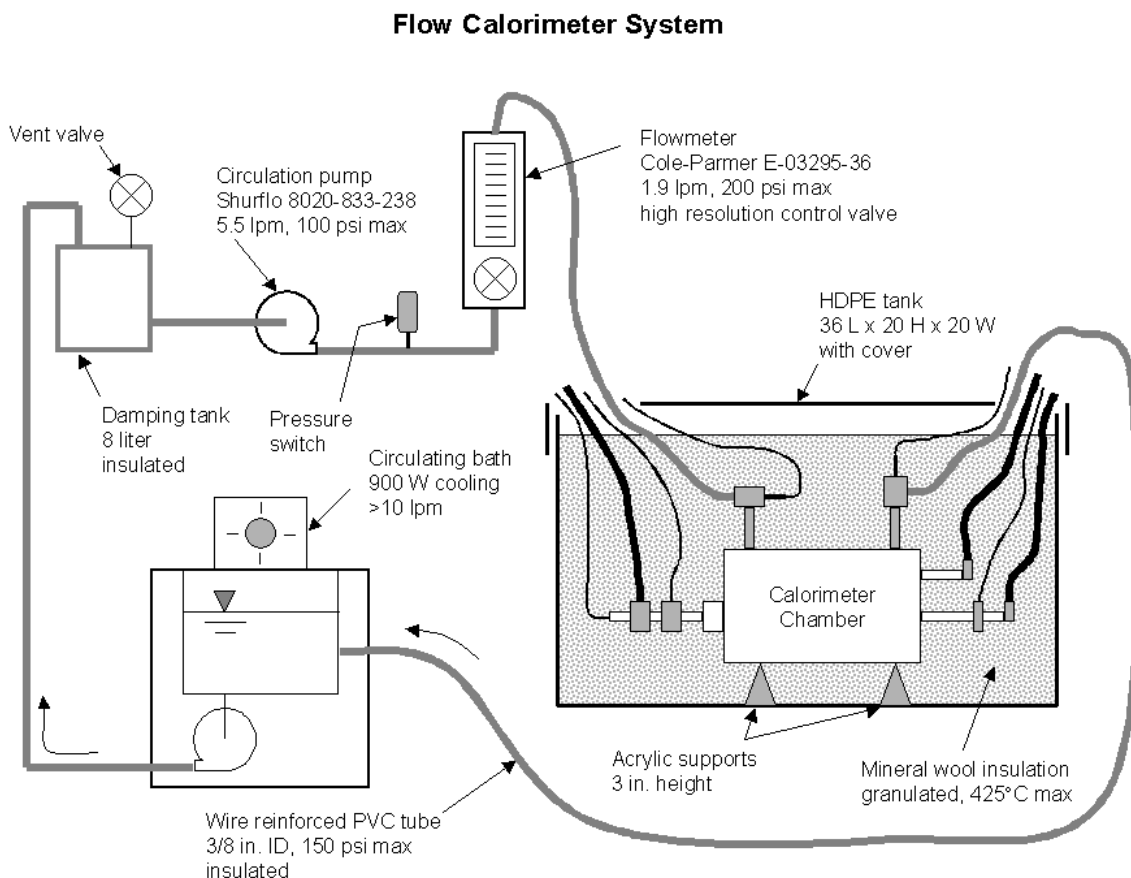


Figure 2. Schematic of the water flow calorimeter used to measure the energy balances.



2.2 Calibration of the calorimeter

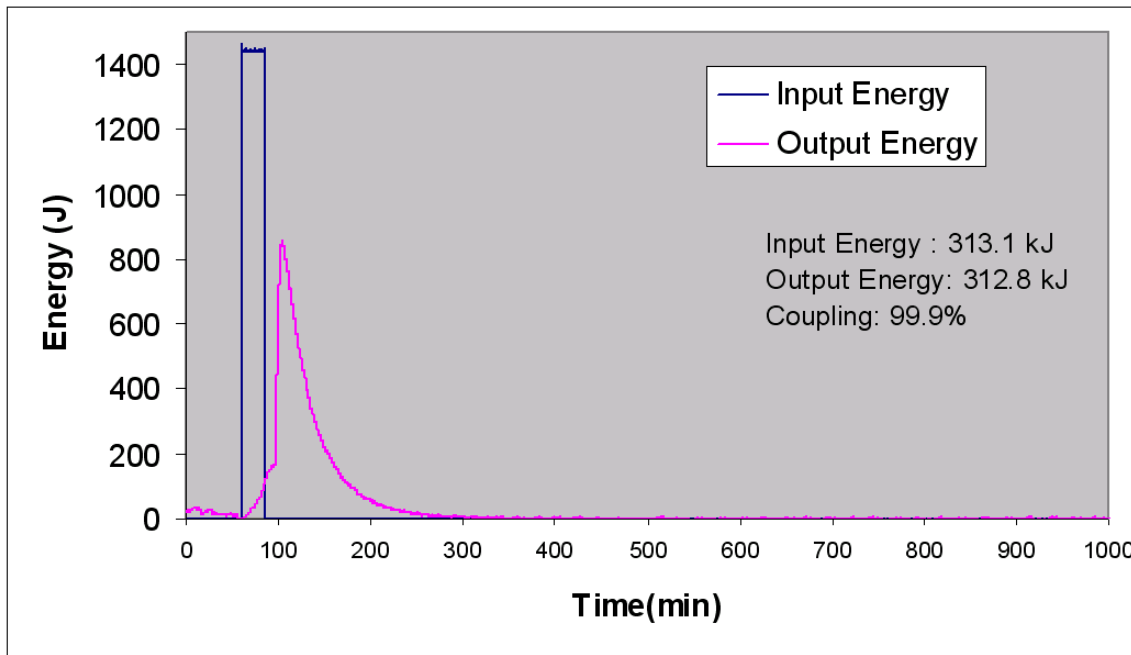
Before running thermal experiments with the chemical systems, the calorimeter was calibrated according to the following procedure.

The empty cell was placed inside the chamber of the standard water flow calorimeter, which was filled with helium and allowed to approach thermal equilibrium, which required approximately one hour. At this point, the cell was evacuated and DC current was applied to the heater generating 200 watts. The cell temperature was measured by a thermocouple inserted into a thermowell in the end of the cylindrical cell. After about 40 minutes, the heater was turned off, and the cell was allowed to reach a peak temperature. Once the peak was reached and temperature decay was observed, helium was added back slowly to the chamber over a period of several minutes using a 1000scm mass flow controller. The pressure was allowed to reach a pressure slightly above atmospheric (typically 850 Torr) as set by the bottle regulator. Under these conditions, heat transfer to the water was increased, and the system approached equilibrium more rapidly. Data acquisition continued for at least 10 hours till the system had clearly reached

equilibrium. Over at least two hours after equilibrium was reached, the inlet and outlet thermistor readings were averaged to estimate the offset relevant for these experiments. For the three cases tested in this visit, the offsets varied within the range $(69.1-71.6) \times 10^{-3} \text{ }^\circ\text{C}$. Water flow rate sensor was calibrated by carefully weighing the amount of water flown during 1-minute period (average of three measurements were used).

The calibration test results shown in Figure 3, demonstrated a very efficient heat coupling of better than 99% of the resistive input to the output coolant, and zero excess heat controls demonstrated that with the calibration correction applied, the calorimeter was accurate to within less than 1% error.

Figure 3. Results of the calorimeter calibration.



3. The system KH+Mg+TiC+MnI₂ run

3.1 Calorimetric experiment and data analysis

Composition of the tested sample is listed in Table 3:

Table 3. Composition of the tested KH+Mg+TiC+MnI₂ sample.

Component	Weight, g
KH	16.64
Mg	10.00
TiC	40.00
MnI ₂	30.90

The cell loaded with the solid fuel sample was placed in the standard water flow calorimeter and the heat experiment was performed following exactly the heater calibration protocol. In this case, a jump in the cell temperature was observed confirming the onset of the reaction and following this input electrical power is turned off. Results of the calorimetric experiment are shown in the Fig. 4 and 5. The numerical integration of the input and output power curves, with the calibration correction applied, yielded output energy of 209 kJ and input energy of 122 kJ. Thus, from Eq. (2), the net energy was 87 kJ. Thus, the calculated theoretical maximum energy for conventional chemistry based on the limiting reagent of 0.1 moles of *MnI₂* is 37.3 kJ for the reaction:



The two XRD results showed products predicted by Eq. (4) at ratios short of the reactants going to completion. Thus, the excess energy and gain (Eq. (3)) were at least 49.7 kJ and 2.3 times the maximum by conventional chemistry given by Eq. (4).

Figure 4. Results of the calorimetric experiment with the system $\text{KH}+\text{Mg}+\text{TiC}+\text{MnI}_2$. The numerical integration of the input and output power curves, with the calibration correction applied, yielded the output energy of 122 kJ and an input energy of 209 kJ corresponding to a net energy of 87 kJ.

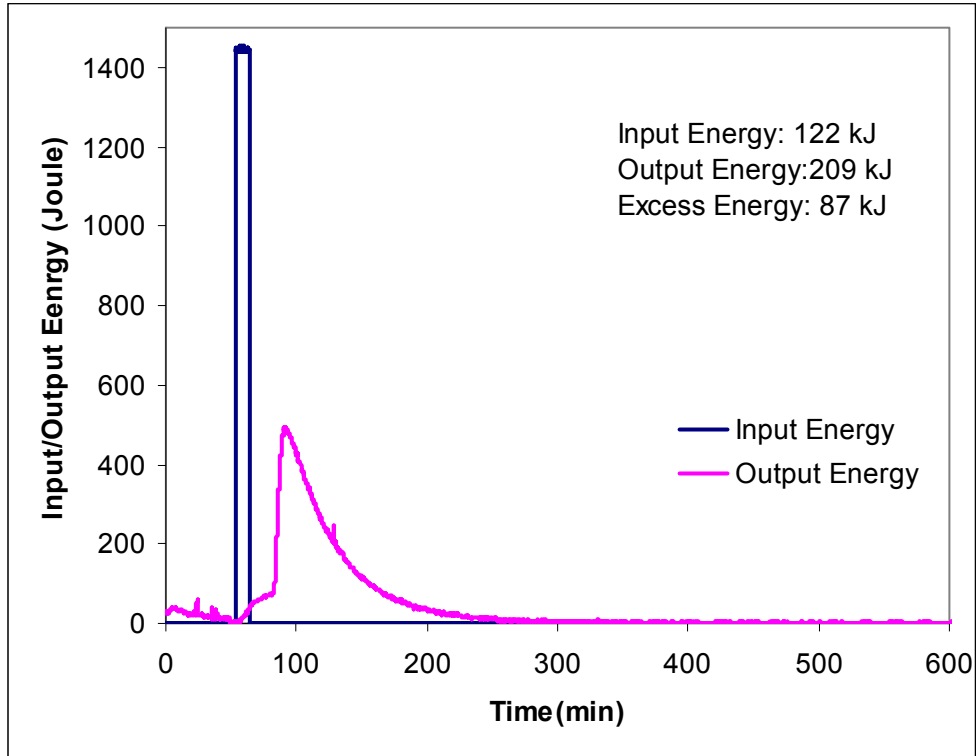
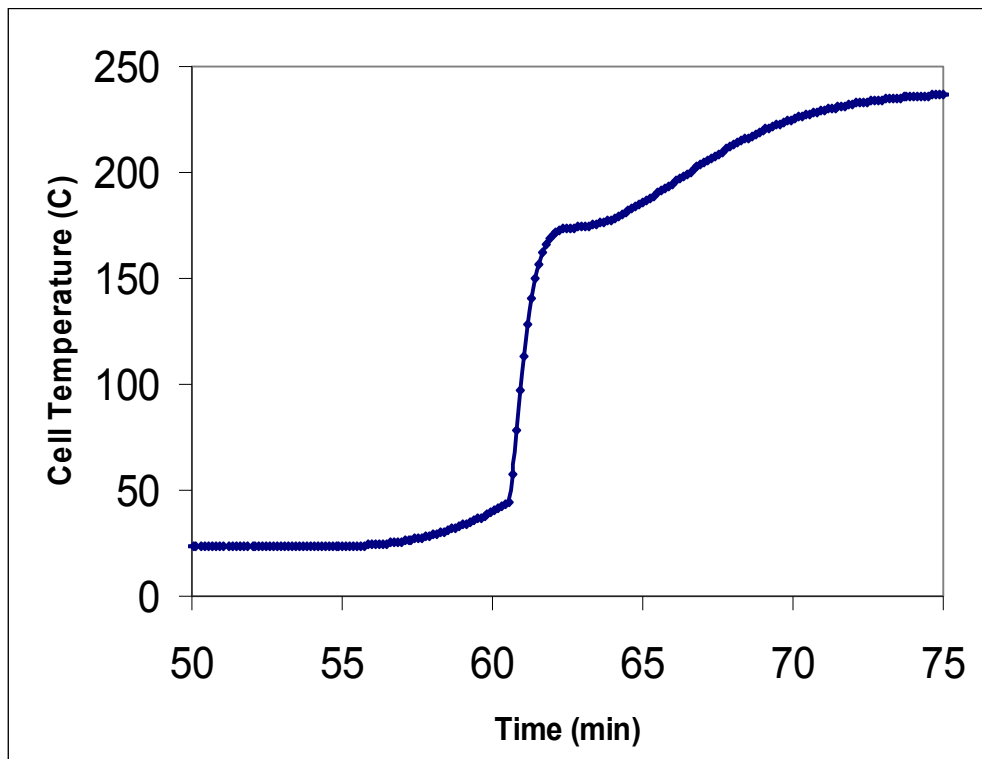


Figure 5. Temporal profile of the cell temperature for the calorimetric experiment with the system KH+Mg+TiC+MnI₂.



3.2 Analysis of the reaction products

Reaction products were analyzed by the methods of mass spectroscopy (MS), gas chromatography (GC) and X-ray diffraction (XRD).

MS

Mass spectrometry identified the constituents of the gas. MS was performed on DYCOR 2000 RGA unit.

GC Analysis

Gas chromatography was used to quantify gas contents in the gas mixture generated in reaction. The analysis was performed on HP 5890II gas chromatography with a thermal conductivity detector (TCD). The gas was directly injected into GC via a six-port rotary valve, which was connected into the gas line right before the injector. Prior to gas sample addition, the sample loop (~3 mL) in six-port rotary valve was sufficiently evacuated ($\sim 10^{-5}$ Torr) to remove any residual gas / contaminant. The amount of gas injected was recorded by a digital pressure gauge (Baratron). A carboxen 1010 plot column (30m x 0.53mm, Supelco) was used for separation with oven temperature at 80 °C. The injector temperature was set at 100 °C, and detector at

120 °C. Helium was the carrier gas, its flow rate was 43.4 mL/min. Chemstation software was employed for GC control and data processing. Calibrations using pure gas H₂, CH₄, Ar, CO, and CO₂ were performed prior to testing.

XRD

The solid sample of post-reaction (extracted from the cell) was pulverized in a mortar and pestle, then carefully packed into a hermetical XRD holder (Brucker AXS). All sample handlings were done in an Ar-filled glove box. The samples in the holder were then placed into a Siemens D5000 diffractometer using Cu radiation at 40KV/30mA. They were run over the normal range of 20° to 60° with a step size of 0.02° and a counting time of 12 hours. Once the patterns of the test samples had been obtained, the phases were identified with the aid of the Powder Diffraction File published by the International Centre for Diffraction Data. This database is the world's most comprehensive source of XRD patterns with over 650,000 entries.

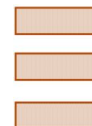
The results obtained are listed in Table 4.

Table 4. Summary of GC, MS, XRD analysis of the products from reaction cell.

ID	Chemicals loaded	Post reaction Cell P (torr), V (mL)	Gas product identification by MS, GC	Gas product quantification (v%)	Solid product by XRD
081809K AWF1	16.64g KH + 10.0g Mg + 40.0g TiC + 30.9 g MnI2	777.8 Torr, 210 mL	CH4, Ar*	8.7% CH4, 91.3% Ar.	KH 1.1 ± 0.2% (>1,000 Å) KI 18.9 ± 0.4% (442 Å) KMgH3 3.7 ± 0.2% (>1,000 Å) K2MgH4 2.3 ± 0.3% (297 Å) Mg 10.6 ± 0.3% (>1,000Å) TiC 63.4 ± 0.7% (301Å)
081809K AWF1-2**	16.64g KH + 10.0g Mg + 40.0g TiC + 30.9 g MnI2	777.8 Torr, 210 mL	CH4, Ar*	8.7% CH4, 91.3% Ar.	KI 31.0 ± 0.3% (485 Å) KMgH3 5.1 ± 0.2% (896 Å) K2MgH4 2.1 ± 0.2% (322 Å) Mg 9.3 ± 0.4% (>1,000Å) MgH2 5.4 ± 0.7% (229 Å) TiC 47.1 ± 0.7% (358Å)
081909K AWF1	8.3g KH + 5.0 g Mg + 20.0g TiC + 15.6g EuBr2	>1000 Torr, 210 mL	H2, CH4, Ar*	80.3%H2, 11.0%CH4, 8.7% Ar.	EuH2 4.2% (751Å) KBr 25.0% (364 Å) KMgH3 3.9% (449 Å) Mg 5.8% (945 Å) MgBr2 0.8% (615 Å) TiC 60.3% (335 Å)

*: Ar is present due to cell loading in Ar-filled drybox.

** : There was a small fraction of solid product in the VCR port, which was suspected to be in cooler zone of the reactor. This fraction (081809KAWF1-2) was separated from the major fraction (081809KAWF1 from cell) and sent for XRD analysis independently. The results of both fractions showed similar content



4. The system KH+Mg+TiC+EuBr₂ run

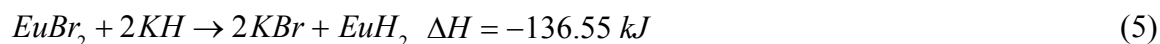
4.1 Calorimetric experiment and data analysis

Composition of the tested sample is listed in Table 5.

Table 5. Composition of the tested KH+Mg+TiC+EuBr₂ sample

Component	Weight, g
KH	8.3
Mg	5.0
TiC	20.0
EuBr ₂	15.6

The cell temperature with time due to the indicated constant power and the coolant power with time for the heterogeneous catalyst mixture, 8.3g $KH(s)$ + 5.0g Mg + 20.0g TiC + 15.6g $EuBr_2$, are shown in Figures 6 and 7, respectively. The numerical integration of input and output power curves, with the calibration correction applied, yielded output energy of 177 kJ and input energy of 130 kJ. Thus, from Eq. (2), the net energy was 47 kJ. The calculated theoretical maximum energy for conventional chemistry based on the limiting reagent of 0.05 moles of $EuBr_2$ is 6.85 kJ for the reaction:



The XRD results showed products predicted by Eq. (5) at ratios short of the reactants going to completion. Assuming completion, the excess energy and gain (Eq. (3)) were 40.15 kJ and 6.8 times the maximum by conventional chemistry given by Eq. (5).

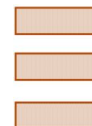
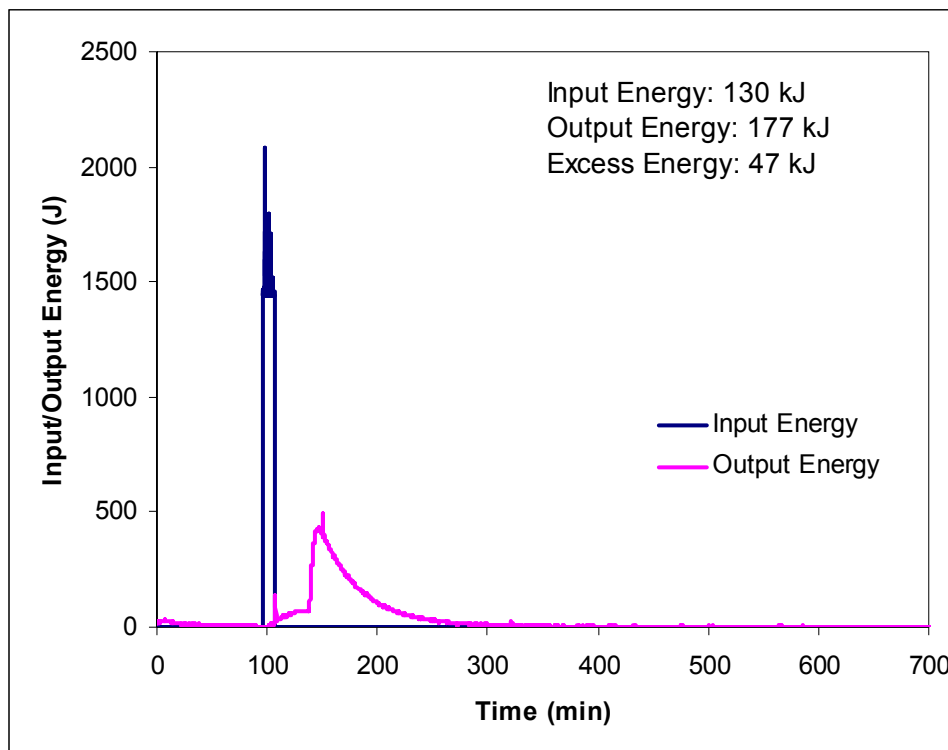


Figure 6. The coolant power with time for the reaction mixture, 8.3g $KH(s)$ + 5.0g Mg + 20.0g TiC + 15.6g $EuBr_2$. The numerical integration of the input and output power curves, with the calibration correction applied, yielded the output energy of 177 kJ and an input energy of 130 kJ corresponding to a net energy of 47 kJ.



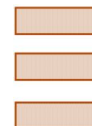
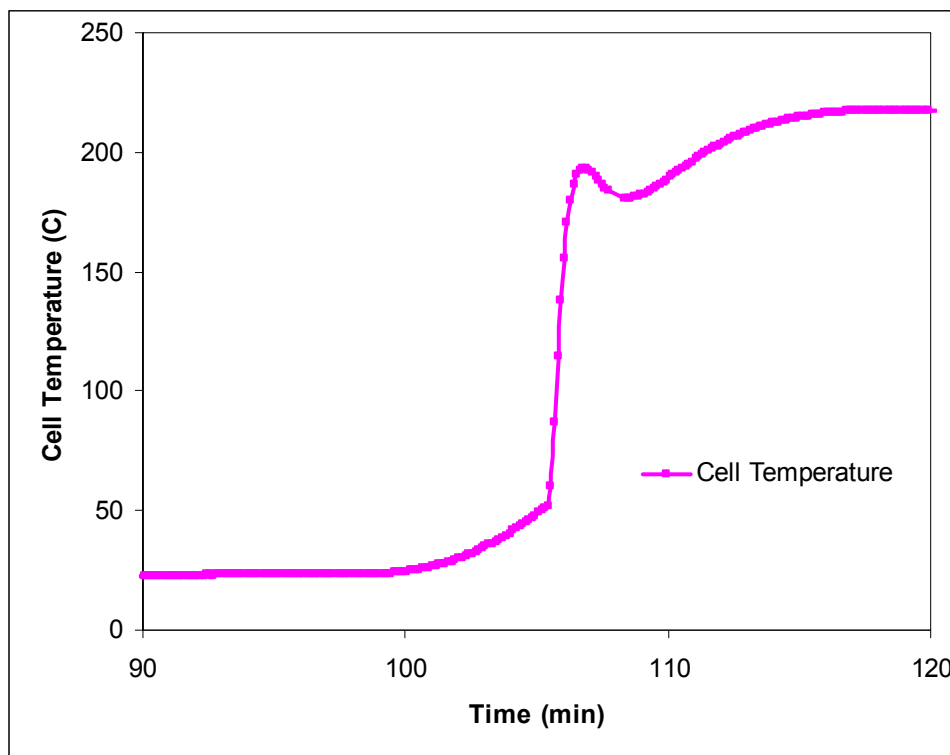


Figure 7. Temporal profile of the cell temperature for the calorimetric experiment with the system $\text{KH}+\text{Mg}+\text{TiC}+\text{EuBr}_2$.



4.2 Analysis of the reaction products

Reaction products were analyzed by the methods of mass-spectroscopy (MS), gas chromatography (GC) and X-ray diffraction (XRD) in the same way as it was described in 3.2. The obtained results are also listed in Table 4.

5. Conclusions and comments

5.1 All procedures were carried out in compliance with those described in previous BLP publications.

5.2 Some additional heat output was recorded during both experiments, which exceeded the total amounts of electric energy input plus energy released from expected exothermic processes in the reaction systems.