

# DESIGN AND TESTING OF A LABVIEW-CONTROLLED CATALYTIC PACKED-BED REACTOR SYSTEM FOR PRODUCTION OF HYDROCARBON FUELS

J. Street, F. Yu, J. Warnock, J. Wooten, E. Columbus, M. G. White

**ABSTRACT.** Gasified woody biomass (producer gas) was converted over a Mo/H<sup>+</sup>ZSM-5 catalyst to produce gasoline-range hydrocarbons. The effect of contaminants in the producer gas showed that key retardants in the system included ammonia and oxygen. The production of gasoline-range hydrocarbons derived from producer gas was studied and compared with gasoline-range hydrocarbon production from two control syngas mixes. Certain mole ratios of syngas mixes were introduced into the system to evaluate whether or not the heat created from the exothermic reaction could be properly controlled. Contaminant-free syngas was used to determine hydrocarbon production with similar mole values of the producer gas from the gasifier. Contaminant-free syngas was also used to test an ideal contaminant-free synthesis gas situation to mimic our particular downdraft gasifier. Producer gas was used in this study to determine the feasibility of using producer gas to create gasoline-range hydrocarbons on an industrial scale using a specific Mo/H<sup>+</sup>ZSM-5 catalyst. It was determined that after removing the ammonia, other contaminants poisoned the catalyst and retarded the hydrocarbon production process as well.

**Keywords.** Gasification, Hydrocarbons, Mo/HZSM-5, Mo/H<sup>+</sup>ZSM-5, Molybdenum catalyst, Oligomerization, Solid acid reaction, Solid alcohol reaction, Syngas, Wood feedstock.

**B**ifunctional catalysts with zeolites can be used to selectively shape carbon chains by creating active sites for oligomerization, alkylation, and isomerization (Fraenkel and Gates, 1980; Street and Yu, 2011). The small porous nanospace found in certain zeolite catalysts controls the growth of the carbon chains that are created (Koh et al., 1995; Lee and Gates, 1992). Studies have shown that the most studied catalysts for Fischer-Tropsch reactions, such as iron, cobalt, nickel, and ruthenium, develop into long-chain hydrocarbons,

which need post-cracking or isomerization to shorten them into liquid fuels. The bifunctional catalyst Mo/H<sup>+</sup>ZSM-5 transforms carbon monoxide and hydrogen into gasoline-range hydrocarbons and does not require any extra energy to crack the hydrocarbons, which would continue to grow if they were only undergoing traditional Fischer-Tropsch chain growth reactions (Liu et al., 2009; Street and Yu, 2011).

A variety of reactor configurations can be used for the liquid hydrocarbon conversion of gasified woody biomass (producer gas). The preferred reactor configuration will give the highest selectivity of gasoline-range hydrocarbons with a minimal temperature variation throughout the reactor. Reactor configurations for the conversion to liquid hydrocarbons include fixed-bed and fluidized-bed reactors (Bukur et al., 1990; Liu et al., 2009; Li et al., 2010; Kang et al., 2011). Both of these types of reactors have advantages and disadvantages. The advantages of a fluidized-bed reactor are that the catalyst particles can be easy to inject and replace. This type of reactor improves the possibility of maintaining an isothermal reactor procedure. Disadvantages of this kind of reactor are that the reactor material requires high mechanical strength, and there is a higher possibility of erosion of the catalyst particles (Mysov et al., 2005). To help control the extreme temperature changes caused by the heat of reaction, fixed-bed multi-tube reactors allow nearly isothermal conditions within the reactor, but this type of system is inconvenient to install in high-capacity industrial plants.

Processes for converting hydrocarbons from methanol and synthesis gas (syngas) include the following reactor types: fluidized-bed reactors, pseudoadiabatic fixed-bed re-

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Submitted for review in January 2012 as manuscript number FPE 9585; approved for publication by the Food & Process Engineering Institute Division of ASABE in May 2012.

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actors, fixed-bed tubular reactors, and monolithic reactors with parallel tubes using catalyst deposits on the walls (Mysov et al., 2005). Efforts to test various reactor configurations could be attempted to find the highest conversion to gasoline-range hydrocarbons and temperature control, but a scaled-up design similar to that used by Liu et al. (2009) was used in this study because of the success of hydrocarbon formation.

The system required the ability to properly maintain and control temperature, flow rate, and pressure to convert syngas into gasoline-range liquid hydrocarbons using a specific catalyst studied by Liu et al. (2009). Liu et al. (2009) discovered that the catalyst 5% Mo/H<sup>+</sup>ZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 50) had a 54% conversion rate of CO at 350°C and a 68% conversion rate of CO at 380°C, which was later reduced to a 62% conversion rate because of catalyst deactivation at 380°C within 20 h on-stream. Although the optimum temperature for production of gasoline-range hydrocarbons using the Mo/H<sup>+</sup>ZSM-5 catalyst for the scale-up of the reactor system may be higher than 350°C, the temperature of 350°C was used in order to keep the catalyst from undergoing deactivation at or near 380°C.

The system was built to have the ability to maintain a certain set point temperature without any major fluctuations. Sustaining certain temperature equilibrium is complicated by the fact that exothermic reactions take place within the reactor. As a result, highly regulated temperature controls and multiple levels of heating of the reactor were used to help maintain a consistent temperature throughout the reactor. Maintaining constant pressure and flow rate on the catalyst is also very important. Pressure highly influences gasoline-range hydrocarbon yields. Because less concentrated levels of CO and H<sub>2</sub> were used in this experiment than were used by Liu et al. (2009), a higher pressure of approximately 1300 psig was used in our system. The producer gas did not consist of pure syngas and had a composition of 19% H<sub>2</sub>, 20% CO, 12% CO<sub>2</sub>, 2% CH<sub>4</sub>, 46% N<sub>2</sub>, and 1% O<sub>2</sub>.

Liu et al. (2009) showed that gasoline-range hydrocarbons were successfully created at a partial pressure of 250 psig for both hydrogen and carbon monoxide. In the current study, a pressure of 1300 psig was used as the total pressure to provide the system with partial pressures of hydrogen and carbon monoxide near the 250 psig required for hydrocarbon production to take place. The CO conversion rate and partial pressure for the CO gas are directly related so that, up to a certain point, the greater the pressure applied to the system, the higher the conversion rate will be, based on the chemical kinetics. This study was used to determine the feasibility of using raw producer gas to create gasoline-range hydrocarbons with Mo/H<sup>+</sup>ZSM-5 catalyst, which is active and selective for direct synthesis of gasoline-range branched and cyclized alkanes as well as aromatic compounds.

## MATERIALS AND METHODS

### REACTOR DESIGN

The packed column reactor tube was assembled using

two cubic 51 mm (2 in.) 316 SS blocks and a 610 mm (24 in.) long 316 SS pipe. Stainless steel was used because it would not react with the syngas and would not rust in the presence of water. Stainless steel is also more cost-efficient compared to other metals of the same strength and can tolerate the temperature profiles of the exothermic reactions. The 316 SS blocks were tapped using 25 mm (1 in.) NPT to be able to attach to the reactor tube, and two 6.4 mm (0.25 in.) NPT taps were used in each block to insert fittings for thermocouple probes to record the temperatures within the reactor. The reactor had a catalyst bed length of approximately 457 mm (18 in.), or a volume of 52.4 mL, to obtain the appropriate gas hourly space velocity (GHSV) using a flow rate of 4.5 standard liters per minute (SLPM), with approximately 102 mm (4 in.) of free space above the top of the catalyst bed to help preheat the syngas before the syngas came in contact with the catalyst. This spacing also helped keep the Teflon tape seal from becoming overheated to the point of failure. Below the catalyst bed was 51 mm (2 in.) of free space to keep the Teflon tape from being overheated. The thermocouple probes in the catalyst bed were spaced every 38 mm (1.5 in.). A horizontal schematic of the reactor is shown in figure 1, but the reactor was used in the vertical position for all experiments.

The catalyst was prepared in the same way as described by Liu et al. (2009). The catalyst bed was supported by a 304 SS wire mesh with a square opening size of 0.23 mm (0.009 in.). Before installation in the reactor, the catalyst was filtered over a 1.6 mm (0.0625 in.) wire mesh, and only the larger remaining particles made up the catalyst bed. The catalyst particles were cut into oblong slabs that ranged in diameter from 3.8 to 6.4 mm (0.15 to 0.25 in.), nearly equivalent to the reactor heuristics of Turton et al. (2009) for a fixed-bed reactor.

Barlow's formula (eq. 1) was used to ensure that the reactor could withstand the pressures and temperatures that were used in the study. The yield strength of 316 SS at a temperature 371°C greater than the maximum temperature used for calcining the catalyst was used to give the greatest safety factor:

$$P = \frac{2St}{D} \quad (1)$$

where  $P$  is the maximum pressure the pipe can handle until the material deforms,  $S$  is the allowable stress (yield stress is used to give the greatest safety factor),  $t$  is the wall thickness of the reactor tube, and  $D$  is the outer diameter of the reactor tube. Using a yield stress of 15,950 psi (316 stainless steel yield stress at 871°C), a wall thickness of 3.9 mm (0.154 in.), and an outer diameter of 26.7 mm (1.050 in.), the internal pressure before deformation would occur was calculated to be 4679.9 psi. This provided a safety factor of approximately 3 with a maximum pressure of 1350 psig in the system (not including the increased estimate in reactor temperature yield stress). To assist with decreasing temperature fluctuations, 13 mm (0.5 in.) thick fiberglass insulation was wrapped around the reactor tube.

In order to remove the heat created from highly exothermic reactions, high rates of heat exchange must be

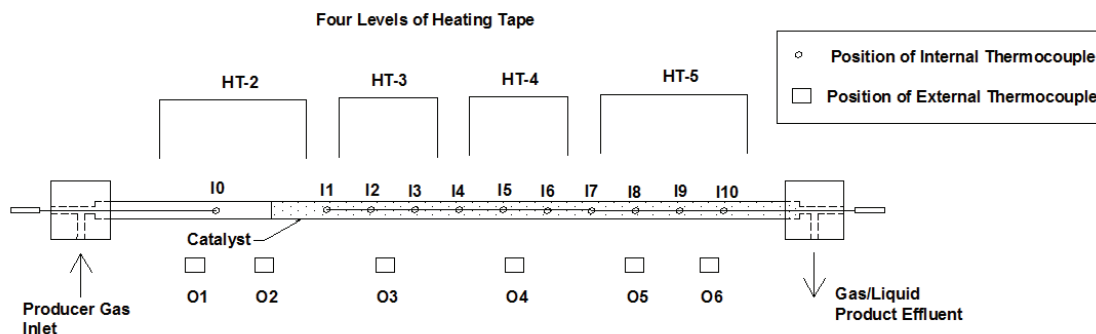


Figure 1. Reactor schematic (shown horizontally, but the reactor was used in the vertical position).

maintained by high flow through the reactor. A near-turbulent flow of syngas through the catalyst is needed to provide this heat exchange so that severe coking and deactivation that result from breaking down of the catalyst's structure can be prevented. The Reynolds number for a packed bed ( $Re_p$ ) is given by equation 2:

$$Re_p = \frac{D_p V_s \rho}{(1 - \epsilon) \mu} \quad (2)$$

where  $D_p$  is the spherical diameter of the packed bed particles,  $\rho$  is the density of the fluid,  $\mu$  is the dynamic viscosity of the fluid,  $V_s$  is the superficial velocity given by equation 3, and  $\epsilon$  is the void fraction of packing given by equation 4:

$$V_s = \frac{Q}{A} \quad (3)$$

where  $Q$  is the volumetric flow rate of the fluid (4.5 SLPM), and  $A$  is the cross-sectional area of the catalyst bed. The catalyst bed diameter was 18.9 mm (0.742 in.).

$$\epsilon = \frac{\rho_b}{\rho_p} \quad (4)$$

where  $\rho_p$  is the particle density, and  $\rho_b$  is the bulk density (the weight of clean material per unit bulk volume as packed in a column).

To properly ascertain the Reynolds number using equation 2, 1 g of Mo/H<sup>+</sup>ZSM-5 zeolite was dropped into a volume of water. To obtain the particle density, the volume of water that was displaced by the catalyst was used to calculate the particle density of 1.67 g mL<sup>-1</sup>. This value compares well with a study by Popescu et al. (2006) wherein the particle densities of modified zeolites were measured. The bulk density was obtained by inserting the 52.4 g of catalyst to be used in the experiments into a glass graduated cylinder to determine the volume. The bulk density was found to be 0.42 g mL<sup>-1</sup>.

The catalyst particles were not perfect spheres, but the value of their diameter, i.e., 6.4 mm (0.25 in.), was used to estimate the Reynolds number. This particle size was used because the mesh used to cut the catalyst into pieces was the approximate diameter of the particle size discussed by

Turton et al. (2009) for reactor heuristics. The Reynolds number was estimated by using the density and dynamic viscosity of air at 315°C and 1000 psi. Based on the above values, the Reynolds number was found to be 9847. This Reynolds number corresponds to a turbulent flow because Rhodes (2008) mentions that, for a packed tube, fully laminar conditions are classified by a Reynolds number less than 10, and fully turbulent flow is maintained at a Reynolds number of 2000 or greater. The scale-up of the reactor system for the efficacy of creating specific hydrocarbons has yet to be studied for this particular catalyst. However, with this Reynolds number, the ability to transfer heat thoroughly throughout the reactor was effective enough to control the exothermic reactions and allow production of liquid hydrocarbons.

## REACTOR FABRICATION

The system was fabricated using 6.4 mm (0.25 in.) 316 SS tubing, two 316 SS tank regulators, two 316 SS ball valves, two 316 SS 15 micron filters, two mass flow controllers (Brooks Instruments, Hatfield, Pa.), two 316 SS check valves, two pressure gauges, two pressure transducers, one 316 SS rupture disk (with a rupture pressure of 1900 psi), two cubic 51 mm (2 in.) 316 SS blocks and one 610 mm (24 in.) 316 SS pipe used for the reactor tube, a 914 mm (36 in.) long coiled condenser made of 6.4 mm (0.25 in.) and 9.5 mm (0.375 in.) 316 SS tubing inserted into an ice/salt bath, one 316 SS sample cylinder 102 mm (4 in.) in diameter and 457 mm (18 in.) long that was used as a gas/liquid separator inside an ice/salt bath, one 316 SS backpressure regulator, one wet test meter (Calibrated Instruments, Hawthorne, N.Y.), one 316 SS needle valve, and one 316 SS pressure-reducing regulator. The equipment for the system was made to withstand pressures far greater than the maximum pressures of the high-pressure tanks used at the beginning of the system.

The LabView software program (National Instruments, Austin, Tex.) was used to read and control the temperature and gas flow rate of the system. The temperature of the heating coils was governed by a relay circuit board controlled by LabView, which read data from the thermocouples on the inside and outside of the reactor.

The process began with syngas flowing through a mass flow controller that regulated the flow. The syngas then

flowed into the reactor to react with the Mo/H<sup>+</sup>ZSM-5 catalyst. Mixed products that formed in the reactor flowed into the condenser and then into the gas/liquid separator, while the wet test meter monitored the gas leaving the system. Gas chromatography was used to determine the composition of the gaseous products leaving the system and determined whether or not liquid products were being created directly after coming in contact with the Mo/H<sup>+</sup>ZSM-5 catalyst. The liquid products were collected periodically using the pressure-reducing regulator.

#### REACTANT AND CATALYST PREPARATION

An online gas chromatograph (GC) was connected with the reactor to measure the formation of hydrocarbons using similar reactor conditions as in a previous study (Liu et al., 2009). Three tests were performed using the producer gas to determine if there were issues with stoichiometric ratios in the gas and if other contaminants (other than the ammonia that was scrubbed) retarded hydrocarbon formation:

Test 1: 40% H<sub>2</sub>, 20% CO, 12% CO<sub>2</sub>, 2% CH<sub>4</sub>, and 26% N<sub>2</sub> (Airgas syngas).

Test 2: 19% H<sub>2</sub>, 20% CO, 12% CO<sub>2</sub>, 2% CH<sub>4</sub>, and 47% N<sub>2</sub> (Airgas syngas).

Test 3: 19% H<sub>2</sub>, 20% CO, 12% CO<sub>2</sub>, 2% CH<sub>4</sub>, 6% N<sub>2</sub>, and 1% O<sub>2</sub> (producer gas).

The catalyst was pretreated with a 50% mole percentage of H<sub>2</sub> and a 50% mole percentage of CO instead of the producer gas to increase the molybdenum carbide and oxide production, as was done by Liu et al. (2009). After the pretreatment, 500 psig of helium was used to purge the system multiple times to flush out any molecules that could have formed in the reactor from the pure H<sub>2</sub> and CO syngas.

The amount of catalyst loaded into the reactor was 125 mL or 52.4 g, and the flow rate was reduced to 4.5 SLPM or a GHSV of 2160 h<sup>-1</sup>. At first, a GHSV of 3000 h<sup>-1</sup> (Liu et al., 2009) was used; however, because of the larger reactor size and the increased capacity of the catalyst, the heat could only be reasonably controlled when the GHSV was reduced. Reduction to a GHSV of 2160 h<sup>-1</sup> increased the total residence time of the syngas in the reactor, which caused greater gasoline-range hydrocarbon selectivity. The overall pressure for each test was increased to 1300 psig to attain the partial pressures of approximately 250 psig reported by Liu et al. (2009) for H<sub>2</sub> and CO in 1:1 tests used to create gasoline-range hydrocarbons. The GC and other equipment used to test the gas and liquid products was the same as used by Street et al. (2012).

#### SOFTWARE LOGIC

A LabView program was created to control and monitor the flow rate of the syngas along with the temperature of the reactor. Multi-element thermocouples were programmed with LabView to account for the exothermic reaction caused by the Mo/H<sup>+</sup>ZSM-5 catalyst. Five independent heating coils were used to keep the reactor at a stable temperature. Multiple arrays were used to read the temperature values at different levels of the reactor. One temperature reading was used for the two grouped thermocouples that were in close proximity to the corresponding heating coil.

The heating coils were turned on or off by the relay switch circuit board based on the temperature of the corresponding thermocouple.

The algorithm in the LabView control program considered rapid temperature changes and adjusted the heating coils accordingly with the use of the relay switch circuit board. If the temperature rose too rapidly, the program turned the heating coils off until the rate of heating was more desirable. If a temperature drop occurred too rapidly near the set point temperature, the program compensated by turning the heating coils on until the rate of cooling became more desirable to help maintain temperature equilibrium. The algorithm was written to maintain relatively close temperature equilibrium, regardless of an exothermic reaction occurring within the reactor.

The flow rates of syngas and helium through the system were also controlled and read into the program. Source code was obtained from Brooks Instruments (Hatfield, Pa.) and implemented in the LabView program to read and control the flow rate into the system using Brooks Instruments mass flow controllers. A pulse generator from Calibrated Instruments along with the wet test meter and a multifunction data acquisition module (USB-600, National Instruments, Austin, Tex.) were used to record the total volume of gases flowing through the meter. This same module was used to record the pressures from transducers before and after the reactor.

#### TEMPERATURE CONTROL

Five rolls of 120 VAC heating tape were used to heat the outside of the reactor. Each tape was 0.61 m (2 ft) long and used 170 W m<sup>-1</sup> (52 W ft<sup>-1</sup>). An RS-232 eight-channel, 10 A, single-pole, double-throw relay switch circuit board (National Control Devices, Osceola, Mo.) was used to control the heating tapes. Five channels were used to accommodate the five heating tapes. Each relay switch controlled the heating tape located on a certain section of the reactor.

Using software from National Control Devices, hexadecimal numbers were recorded to specify the input commands used to turn a specific relay switch channel off or on. These command values were used in LabView along with an algorithm to keep the temperature at the specified set point. Five universal serial bus (USB) data acquisition modules (model USB-9162, National Instruments, Austin, Tex.) were used to determine the temperature on the inside and outside of the reactor.

Eleven type-K thermocouples (Omega Engineering, Stamford, Conn.) were used to measure the temperature inside the reactor. One thermocouple (identified as I0 in fig. 1) recorded the temperature of the syngas in the 102 mm (4 in.) long top portion of the reactor before the syngas made contact with the catalyst. The other ten thermocouples inside the reactor were spaced every 38 mm (1.5 in.), as measured from the tip of the thermocouple probe. Six thermocouples were located on the outside of the reactor (fig. 1).

The reactor was divided into four sections (fig. 1) plus the preheater, which corresponded to five relay switch channels. A simple algorithm was written to turn each heat-

ing tape on or off in response to a change in temperature in the corresponding section of the reactor. Five thermocouples were used with the feedback loop in the LabView program to cause relay switch channels to turn on the heating tape that corresponded to the appropriate section of the reactor. These thermocouples are identified as I1, I2, I3, I5, and I7 in figure 1. A reading was recorded every 2 s, and the logic portion of the algorithm decided to turn a specific heating coil on or off.

The first relay switch channel corresponded to thermocouple I1. This relay switch acted as a preheater because it controlled the heating tape on a section of tubing before the syngas reached the reactor. This heating tape was activated by the first relay switch if the top of the catalyst bed temperature, with an addition of 50°C, was lower than the set point temperature. If the temperature in the top of the catalyst bed, with an addition of 50°C, was higher than the set point temperature, then the first relay switch turned off the heating tape. The first relay switch channel's Boolean logic is given by equation 5:

$$\text{Top of catalyst bed temperature} + 50^{\circ}\text{C} < \text{Set point temperature} \quad (5)$$

If this statement was true, then preheating occurred; if it was false, then no preheating occurred.

The second through fifth relay switch channels controlled the four sections of the reactor. The second relay channel corresponded with heating the section of the reactor containing the top portion of the catalyst and is identified as HT-2 in figure 1. This relay switched the heating tape on and off based on an array of temperatures that were collected. Every 2 s, a temperature reading was collected from thermocouple I2 (fig. 1), and this reading was inserted into an array. The reading was inserted into index position 0, and the previous reading was inserted into the next index of the array. An algorithm was written to accommodate the extreme exothermic reaction that took place by turning off the heating tape if the temperature was within 10°C of the set point temperature or if the increase in temperature from one index to another in the array was too large. If the increase in temperature was greater than 0.25°C for a 2 s period, the set point temperature was automatically decreased by 100°C within the program so that if the current temperature was within 100°C of the user's set point, the relay switch would turn off the heating tape. If the increase in temperature was greater than 0.30°C for a 2 s period, the set point temperature was automatically decreased by 200°C within the program so that if the current temperature was within 200°C of the user's set point, the relay switch would turn off the heating tape for that section of the reactor.

Another part of the algorithm was written to accommodate the cooling of the reactor. If the temperature was above the user's set point and then started to drop so that the decrease in temperature from one index to another in the array was too large and a specified value away from the set point temperature, the heating tape would be turned on. If the decrease in temperature was greater than 0.20°C for a 2 s period, the set point temperature was automatically in-

creased by 5°C within the program so that if the current temperature was within 5°C of the user's set point, the relay switch would turn on the heating tape. If the decrease in temperature was greater than 0.25°C for a 2 s period, the set point temperature was automatically increased by 10°C within the program so that if the current temperature was within 10°C of the user's set point, the heating tape was switched on for that section of the reactor.

The third relay channel corresponded with heating the section of the reactor containing the middle portion of the catalyst and is identified as HT-3 in figure 1. Every 2 s, a temperature reading was collected from thermocouple I3 (fig. 1), and this reading was inserted into an array. The heating and cooling algorithm was similar to the algorithm that controlled the second relay channel, with the difference that if the increase in temperature was greater than 0.25°C for a 2 s period, the set point temperature was automatically decreased by 200°C within the program so that if the current temperature was within 200°C of the user's set point, the relay switch would turn off the heating tape. If the increase in temperature was greater than 0.30°C for a 2 s period, the set point temperature was automatically decreased by 300°C within the program so that if the current temperature was within 300°C of the user's set point, the relay switch would turn off the heating tape for that section of the reactor. This algorithm was different from the second relay channel because, after many preliminary tests, it was shown that this section of the reactor was more active in the exothermic reaction. Therefore, the warming of this section of the reactor was slowed to keep the reactor from rapidly heating to the point of a runaway reaction.

The fourth relay channel corresponded with heating the section of the reactor containing the lower-middle portion of the catalyst and is identified as HT-4 in figure 1. Every 2 s, a temperature reading was collected from thermocouple I5 (fig. 1), and this reading was inserted into an array. The heating and cooling algorithm for this relay channel was the same as the algorithm that controlled the second relay channel.

The fifth relay channel corresponded with heating the section of the reactor containing the lowest portion of the catalyst and is identified as HT-5 in figure 1. Every 2 s, a temperature reading was collected from thermocouple I7 (fig. 1), and this reading was inserted into an array. The heating and cooling algorithm was similar to the algorithm that controlled the second relay channel, with the difference that if the increase in temperature was greater than 0.35°C for a 2 s period, the set point temperature was automatically decreased by 100°C within the program so that if the current temperature was within 100°C of the user's set point, the relay switch would turn off the heating tape. If the increase in temperature was greater than 0.40°C for a 2 s period, the set point temperature was automatically decreased by 200°C within the program so that if the current temperature was within 200°C of the user's set point, the relay switch would turn off the heating tape for that section of the reactor. This algorithm was different from the second relay channel because, after many preliminary tests, it was shown that this section of the reactor was less active in the exothermic reaction. Therefore, a different rate of tempera-

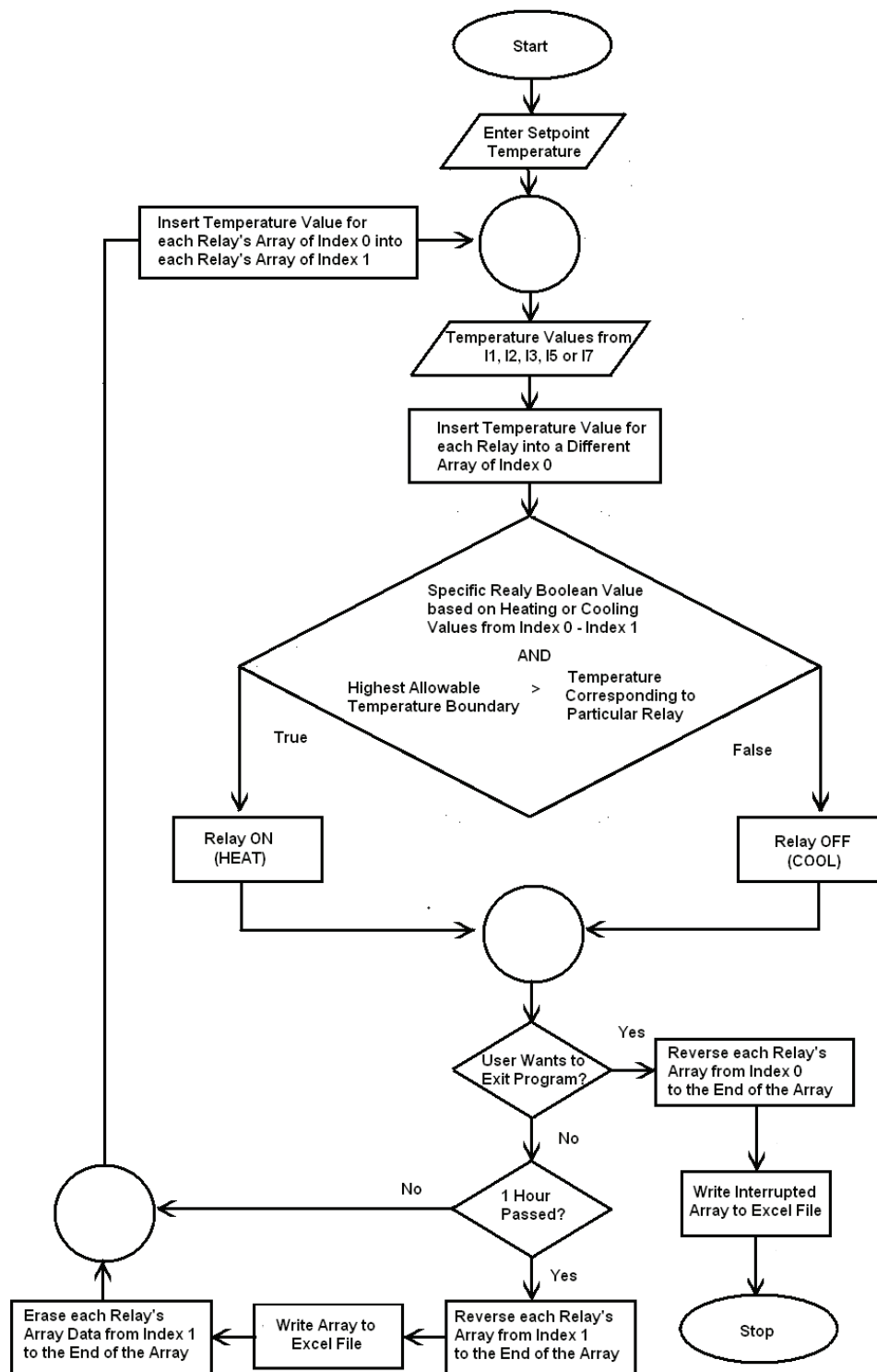


Figure 2. Simplified flowchart of the temperature control algorithm.

ture increase was used in the algorithm as a means of keeping the reactor temperature equilibrated. A simplified flow diagram of the temperature control program using the specific Boolean values mentioned above can be seen in figure 2.

The graphical user interface (GUI) displayed whether or not the reactor was heating or cooling in certain sections based on the array of temperature data collected from each

thermocouple. Each relay channel's setting was controlled by the overall temperature of the system. The user input a temperature, known as the "highest allowable temperature," into the GUI, which turned off all the relay channels if the temperature for any of the thermocouples reached this user-specified temperature.

Temperature warnings were given based on user preferences. An input in the GUI known as the "allowable inside

temperature” warned the user if the inside of the reactor was too hot or too cold based on the upper seven thermocouples inside the reactor that were in contact with the catalyst (I1 through I7 in fig. 1). This warning used the set point temperature as the baseline value. Once the temperature was near the set point, the user could change the warning value to indicate if the temperature was too hot or cold based on the difference between the set point temperature and the temperature reading of a thermocouple. Two warnings, in the form of two different sounds, were used for this purpose. In addition, the green light in the GUI under “too hot” turned red if the reactor was too hot, and the green light in the GUI under “too cold” turned blue if the reactor was too cold.

The user also had the ability to input a value in the GUI known as the “allowable outside temperature.” This value warned if the outside of the reactor was too hot based on the six thermocouples on the outside of the reactor, as shown in figure 1. If the temperature on the outside of the reactor was higher than the user-specified “highest allowable temperature,” a green warning light turned red. In addition, a specific sound cautioned the user that the outside of the reactor was too hot.

#### FLOW CONTROL

The syngas and helium flow controllers were controlled by proportional-integral-derivative (PID) software obtained from Brooks Instruments. The software source code was modified to allow implementation of the heating control and the flow control program to coincide within the LabView program. The software allowed the user to input a flow rate in standard liters per minute (SLPM), and this information was related to the control box (model 0154, Brooks Instruments, Hatfield, Pa.). The control box communicated with each of the flow controllers, which regulated the flow rate of the syngas.

#### COMPUTER MEMORY ALLOCATION

Memory allocation was important to keep the computer from getting overloaded with data to the point that it caused a system crash. The LabView program created a Microsoft Excel file for the date, the current time, the amount of time (in hours, minutes, and seconds), the number of seconds that elapsed from the start of an experimental run, the eleven thermocouples on the inside of the reactor, the six thermocouples on the outside of the reactor, the thermocouple relating to the condenser temperature, the thermocouple relating to the temperature inside the wet test meter, information regarding the total volume of gas that passed through the wet test meter, information regarding whether or not the five relay switches for the heating tapes were on or off, the pressure before the reactor, and the pressure after the reactor. These data were stored every 2 s in the computer’s memory. Each hour, these data were stored into a separate Excel file, which allowed the computer to erase the data that was stored in memory for that hour. The flow rates of syngas and helium were stored in the same way and were output into separate Excel files.

Consideration for an interruption of the experiment was also provided. If the program was interrupted before a full

hour was reached, the data currently held in the computer’s memory from the interrupted experiment were written to an Excel file so that the data for the experiment would not be lost.

#### SAFETY EMPHASIS

The biggest safety concern for this research project was the hazardous gas carbon monoxide. Checking for leaks in the system and keeping a carbon monoxide meter near the lab workstation were precautions undertaken to avoid health problems. In future work, this issue will be addressed by interfacing a carbon monoxide meter with the LabView program to provide a warning and even stop the flow of syngas if carbon monoxide levels become too high.

Working with gas pressures near 1500 psig also presents a hazard. If measures are not taken to ensure that the materials used can tolerate the temperatures and pressures in the experiment, dire consequences can occur. The tubing, valves, fittings, mass flow controllers, filters, meters, regulators, and sample cylinder were all carefully examined to ensure that they could handle the pressures required for this study. This was done to ensure that no harm would be done to the operators or the equipment. The rupture disc included in the system also contributed to the safety of the experiment.

## RESULTS AND DISCUSSION

#### TESTING OF THREE DIFFERENT GAS MIXES USING $\text{Mo}/\text{H}^+\text{ZSM-5}$ CATALYST

To test an ideal situation, a clean syngas (Airgas) 2:1 mole ratio of  $\text{H}_2$  to CO (40%  $\text{H}_2$ , 20% CO, 12%  $\text{CO}_2$ , 2%  $\text{CH}_4$ , and 26%  $\text{N}_2$ ) was used to show the maximum amount of liquid products that could be obtained under ideal stoichiometric reactions with a mole ratio of gases closely related to that of the downdraft gasifier. To test an ideal contaminant-free situation for our particular downdraft gasifier, a clean syngas (Airgas) mix equivalent to the mole ratio of the gasifier was obtained. This mix was a nearly 1:1 mole ratio of  $\text{H}_2$  to CO (19%  $\text{H}_2$ , 20% CO, 12%  $\text{CO}_2$ , 2%  $\text{CH}_4$ , and 47%  $\text{N}_2$ ). The mole ratio percentages (19%  $\text{H}_2$ , 20% CO, 12%  $\text{CO}_2$ , 2%  $\text{CH}_4$ , 46%  $\text{N}_2$ , and 1%  $\text{O}_2$ ) from the gasifier were tested after being put through a water scrubber. Unlike the clean syngas, the producer gas mix contained certain impurities, such as  $\text{O}_2$ ,  $\text{NO}_x$ , and ammonia. Ammonia was produced from the gasification process and poisoned the acid sites of the catalyst to retard or prevent hydrocarbon formation (Norton and Brown, 2005; Street and Yu, 2011).

The minimum and maximum temperature values ( $^{\circ}\text{C}$ ) for each internal thermocouple (I2 through I7 in fig. 1) using the 2:1 syngas, 1:1 syngas, and 1:1 producer gas are shown in figures 3, 4, and 5, respectively, over the 9 h period that the syngas was in contact with the catalyst. The figures show testing that was done in three replicates for each gas mix. The temperature set point was  $350^{\circ}\text{C}$  for all three replicates, and table 1 shows the minimum and maximum temperature values for each gas mix. Figures 3, 4, and 5 with table 1 show that the 2:1 syngas was the furthest from



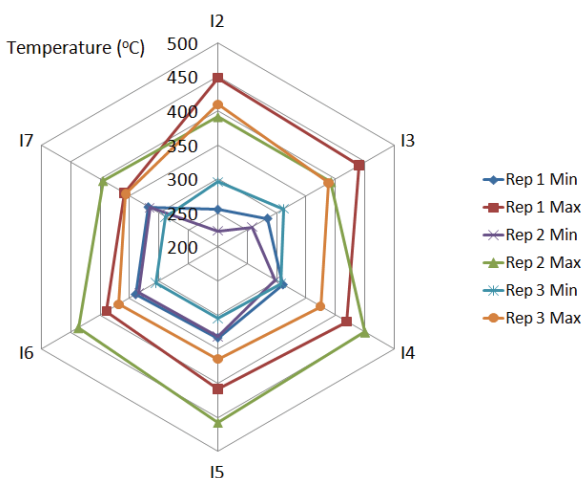


Figure 3. 2:1 Airgas syngas minimum and maximum internal temperatures with three repetitions over Mo/H<sup>+</sup>ZSM-5 catalyst.

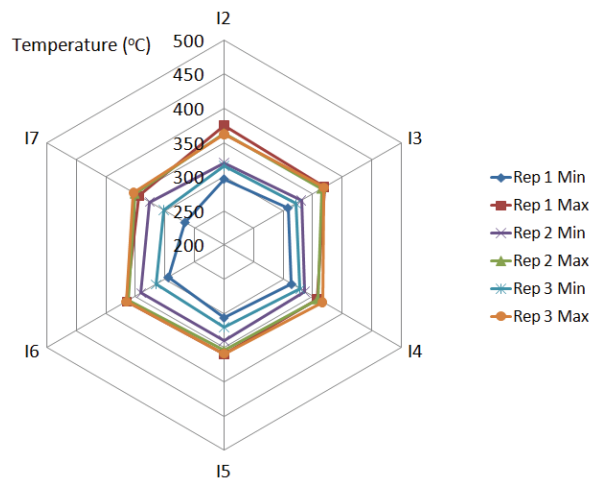


Figure 5. 1:1 Producer gas minimum and maximum internal temperatures with three repetitions over Mo/H<sup>+</sup>ZSM-5 catalyst.

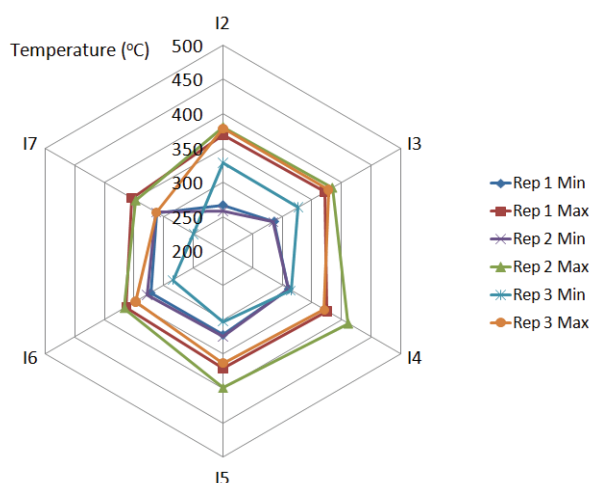


Figure 4. 1:1 Airgas syngas minimum and maximum internal temperatures with three repetitions over Mo/H<sup>+</sup>ZSM-5 catalyst.

Table 1. Minimum and maximum internal temperatures of three replicates.

Gas	Minimum (°C)	Maximum (°C)
2:1 Syngas	223.5	457.4
1:1 Syngas	249.6	411.3
Producer gas	266.2	374.7

ing the ammonia (based on infrared spectroscopy).

Table 2 shows the CO conversion rate and the selectivity to different hydrocarbons of the three gas mixes. The results showed that the selectivity to carbon dioxide for the producer gas was much greater than for the two syngas mixes. This is due to the fact that the producer gas had contaminants that the other two syngas mixes did not have. The 2:1 and 1:1 syngas mixes both produced a greater amount of gasoline-range hydrocarbons than the producer gas. The partial pressure of H<sub>2</sub> in the 2:1 syngas was nearly double that of the 1:1 syngas. The stoichiometric ratio of the 2:1 syngas to hydrocarbons was a more effective condition for creating hydrocarbons than the 1:1 syngas mix, as can be seen in table 2.

## LIQUID AND GAS RESULTS

After testing the producer gas over the Mo/H<sup>+</sup>ZSM-5 catalyst at a temperature of 350°C, the results showed that hydrocarbon peaks were created at the beginning of the test. However, at about 4 h into the test, these peaks became less pronounced and finally disappeared. The producer gas was analyzed, and 4 ppm of ammonia was found. The producer gas was then scrubbed with water using a pressure dispensing tank (McMaster-Carr, Aurora, Ohio). The 95 L (25 gal) pressure dispensing tank was filled with water, and the producer gas was compressed to 50 psig. The producer gas flowed through the tank at a flow rate of 110 SLPM, and this scrubber was 100% efficient in remov-

## CONCLUSION

This packed-bed reactor system was able to monitor and control the temperature and flow rate of syngas and producer gas through the Mo/H<sup>+</sup>ZSM-5 catalyst, but creating a catalyst that produced a less exothermic reaction as well as programming that can more precisely control the temperature would be more ideal. The LabView control program provided the ability to control and maintain the flow rate and temperature to produce specific hydrocarbons from biomass feedstock gasified using a downdraft gasifier. The

Table 2. Catalytic performance of Mo/H<sup>+</sup>ZSM-5 on three different gas mixes.

Gas	CO Conversion Rate (%)	Selectivity (%) <sup>[a]</sup>					
		CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> -H <sub>x</sub>	C <sub>3</sub> -H <sub>x</sub>	C <sub>4</sub> -H <sub>x</sub>	C <sub>n</sub> <sup>+</sup> -H <sub>x</sub>
2:1 Syngas	15.20 ± 2.10	28.69 ± 5.17	24.09 ± 3.07	36.50 ± 4.39	11.22 ± 2.88	12.46 ± 1.31	0.12 ± 0.06
1:1 Syngas	10.26 ± 0.71	29.30 ± 2.24	20.81 ± 3.06	22.86 ± 0.14	8.79 ± 0.43	10.11 ± 0.91	0.06 ± 0.02
Producer gas	10.43 ± 0.85	69.95 ± 0.87	14.36 ± 1.77	9.23 ± 1.47	10.08 ± 5.31	12.07 ± 4.60	0.01 ± 0.01

<sup>[a]</sup> Selectivity is based on number of atoms per gram of carbon = (number of CO converted to given product)/(total number of CO converted) × 100%. H<sub>x</sub> is for multiple hydrogen atoms; C<sub>n</sub><sup>+</sup>-H<sub>x</sub> includes gasoline-range hydrocarbons where n ≥ 5. Reaction conditions: P = 1000 psi, GHSV = 2000 h<sup>-1</sup>.



experiments showed that, by having a Reynolds number of 9847 with help of the inert gas nitrogen and with multiple heating sections on the reactor, the reactor heat could be adequately controlled as the syngas underwent exothermic reactions due to the Mo/H<sup>+</sup>ZSM-5 catalyst. The reactor achieved the set point temperature, but the exothermic reactions caused the internal temperature to increase while the external temperature dropped dramatically. This was necessary to cool the reactor, but the reactor then needed time to heat up to maintain the desired temperature. The reactor temperature fell below the desired value before heating back up, and the exothermic reactions caused the reactor temperature to overshoot the set point.

Increasing the GHSV of the syngas would increase the amount of syngas passing through the catalyst and therefore increase liquid hydrocarbon production, but this would also cause problems with temperature control. The GHSV can be increased if the temperature can be more adequately controlled. Controlling the temperature would be better accomplished by using cooling throughout the inside of the reactor and by using a material with a high thermal conductivity to dissipate the excess heat. Cooling could also be accomplished with a shell-and-tube type heat exchanger design for the reactor. Future values of temperature, pressure, and GHSV can be tested with further modification of the reactor cooling system and alterations of the temperature algorithm to discover the optimum variables to produce the maximum amount of specific gasoline-range liquid hydrocarbons.

#### ACKNOWLEDGEMENTS

This material is based on work performed through the Sustainable Energy Research Center at Mississippi State University and is supported by the Department of Energy (Awards DE-FG3606GO86025 and DE-FC2608NT01923) and the USDA (Award AB567370MSU).

#### REFERENCES

Bukur, D. B., S. A. Patel, and X. Lang. 1990. Fixed bed and slurry reactor studies of Fischer-Tropsch synthesis on precipitated

- iron catalyst. *Applied Catalysis* 61(1): 329-349.
- Fraenkel, D., and B. C. Gates. 1980. Shape-selective Fischer-Tropsch synthesis catalyzed by zeolite-entrapped cobalt clusters. *J. American Chem. Soc.* 102(7): 2478-2480.
- Kang, S., J. W. Bae, J. Cheon, Y. Lee, K. Ha, K. Jun, D. Lee, and B. Kim. 2011. Catalytic performance on iron-based Fischer-Tropsch catalyst in fixed-bed and bubbling fluidized-bed reactor. *Applied Catalysis B* 103(1-2): 169-180.
- Koh, D. J., J. S. Chung, and Y. G. Kim. 1995. Selective synthesis and chain growth of linear hydrocarbons in the Fischer-Tropsch synthesis over zeolite-entrapped cobalt catalysts. *Ind. and Eng. Chem. Res.* 34(6): 1969-1975.
- Lee, T. J., and B. C. Gates. 1992. Rhodium in basic zeolite Y: A stable, selective catalyst for CO hydrogenation. *J. Molecular Catalysis* 71(3): 335-346.
- Li, Y., T. Wang, C. Wu, H. Li, X. Qin, and N. Tsubaki. 2010. Gasoline-range hydrocarbon synthesis over CO/SiO<sub>2</sub>/HZSM-5 catalyst with CO<sub>2</sub>-containing syngas. *Fuel Proc. Tech.* 91(4): 388-393.
- Liu, S., A. C. Gujar, P. Thomas, H. Toghiani, and M. G. White. 2009. Synthesis of gasoline-range hydrocarbons over Mo/HZSM-5 catalysts. *Applied Catalysis A* 357(1): 18-25.
- Mysov, V. M., S. I. Reshetnikov, V. G. Stepanov, and K. G. Ione. 2005. Synthesis gas conversion into hydrocarbons (gasoline range) over bifunctional zeolite-containing catalyst: Experimental study and mathematical modelling. *Chem. Eng. J.* 107(1-3): 63-71.
- Norton, G. A., and R. C. Brown. 2005. Wet chemical method for determining levels of ammonia in syngas from a biomass gasifier. *Energy and Fuels* 19(2): 618-624.
- Popescu, V., C. Oprea, and S. Birghila. 2006. Chemical modified zeolites. *Romanian J. Physics* 51(1-2): 293-298.
- Rhodes, M. J. 2008. *Introduction to Particle Technology*. West Sussex, U.K.: John Wiley and Sons.
- Street, J., and F. Yu. 2011. Production of high-value products including gasoline hydrocarbons from the thermochemical conversion of syngas. *Biofuels* 2(6): 677-991.
- Street, J., F. Yu, J. Wooten, E. Columbus, M. G. White, and J. Warnock. 2012. Gasoline-range hydrocarbon production using biomass-derived synthesis gas over Mo/H<sup>+</sup>ZSM-5. *Fuel* 96: 239-249.
- Turton, R., R. C. Bailie, W. B. Whiting, and J. A. Shaeiwitz. 2009. *Analysis, Synthesis, and Design of Chemical Processes*. 3rd ed. Upper Saddle River, N.J.: Prentice Hall.