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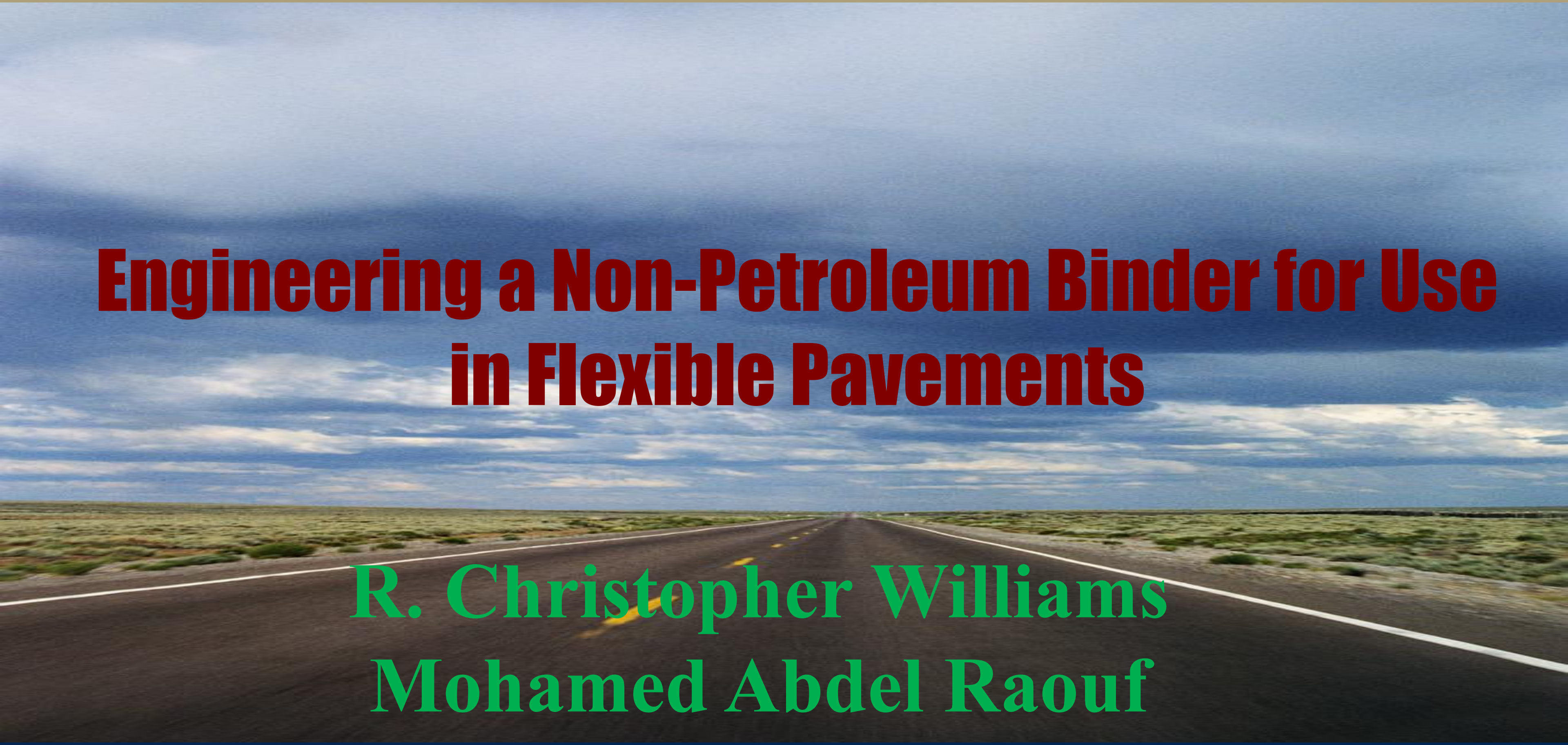


Engineering a Non-Petroleum Binder for Use in Flexible Pavements

R. Christopher Williams
Mohamed Abdel Raouf

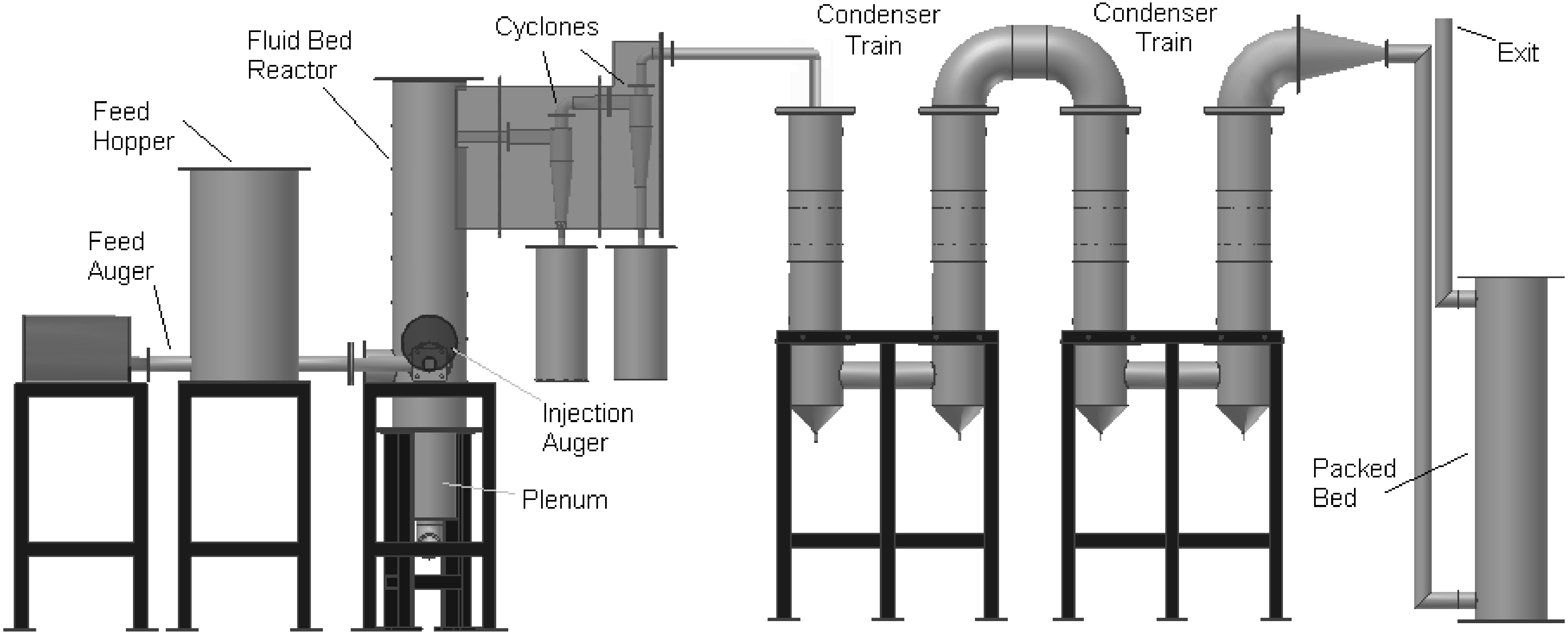
Presentation Outline

- Production of bio-oils and characteristics
- Experimental plan and upgrading of bio-oil
- Characteristics of bio asphalt
- Environmental Opportunities
- Summary/Conclusions
- Ongoing and next steps in research

Impetus for Research

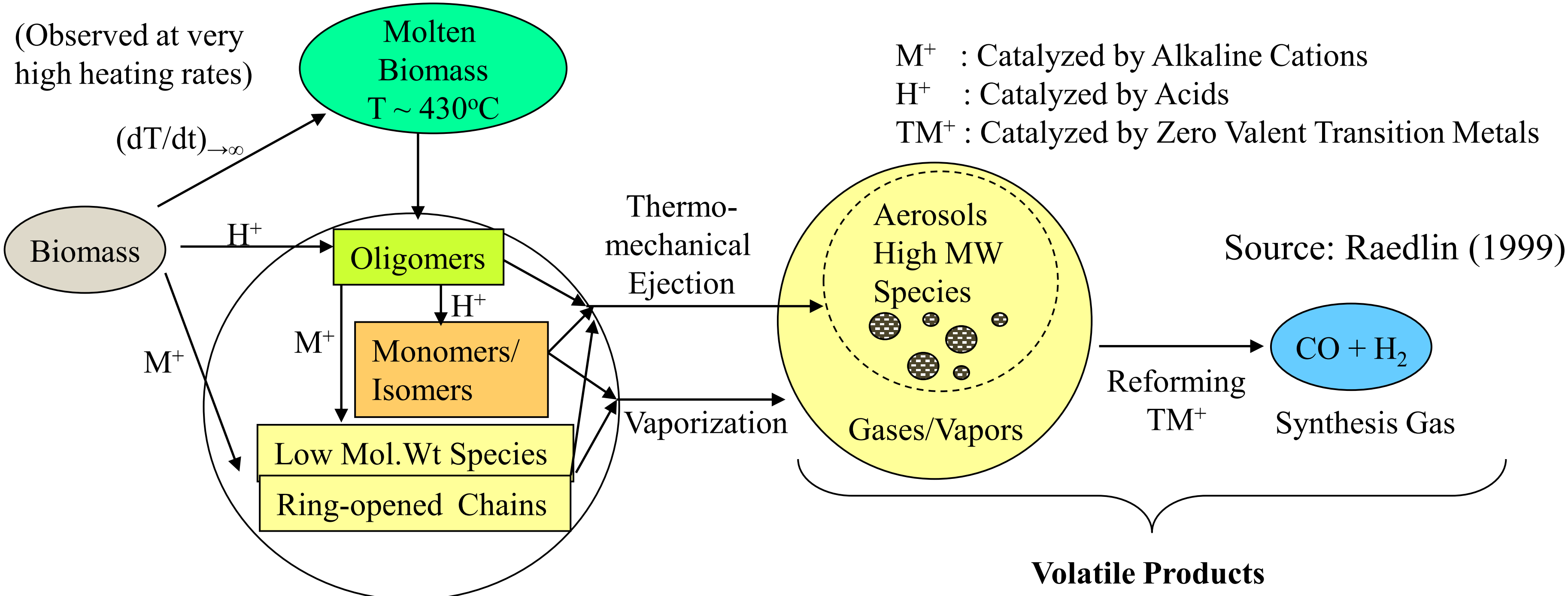
- Developing bio-economy
- Link between bio-economy and transportation infrastructure
- Renewable sources of materials
- Economic opportunity

Fast Pyrolysis



Fast pyrolysis - rapid thermal decomposition of organic compounds in the absence of oxygen to produce gas, char, and liquids

- Liquid yields as high as 78% are possible for relatively short residence times (0.5 - 2 s), moderate temperatures (400-600 ºC), and rapid quenching at the end of the process



(Observed at very high heating rates)

Molten Biomass $T \sim 430^oC$

$(dT/dt)_{\rightarrow\infty}$

Biomass

H^+

Oligomers

H^+

M^+

M^+

Monomers/ Isomers

Low Mol.Wt Species

Ring-opened Chains

Thermo-mechanical Ejection

Vaporization

Aerosols High MW Species

Gases/Vapors

Reforming TM^+

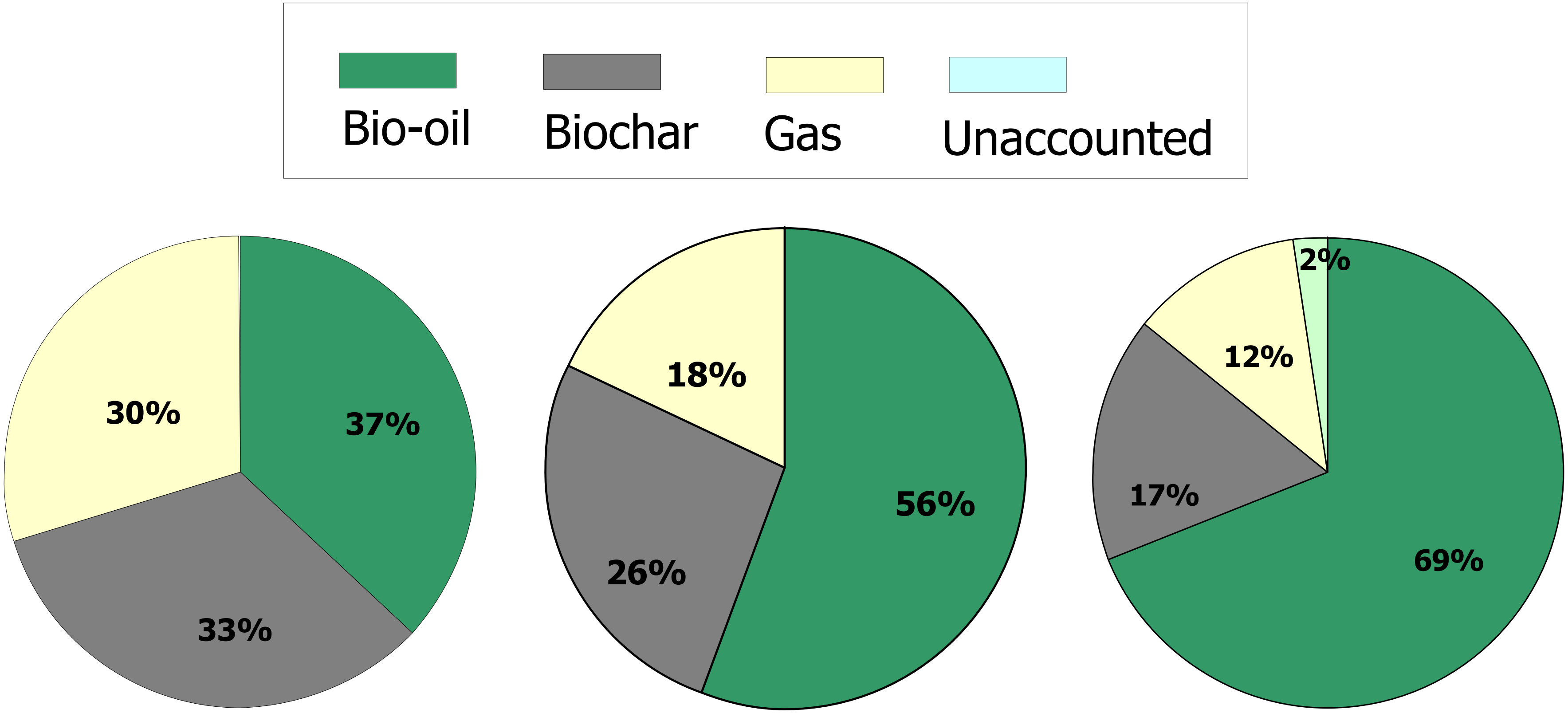
$CO + H_2$

Synthesis Gas

Volatile Products

M^+ : Catalyzed by Alkaline Cations
H^+ : Catalyzed by Acids
TM^+ : Catalyzed by Zero Valent Transition Metals

Source: Raedlin (1999)



Corn stover (0.5-1.0mm)
10 run average, different conditions
$\sigma_{\text{bio-oil}} = 6.09\%$; $\sigma_{\text{char}} = 8.27\%$

Corn fiber (1.0 mm)
2 run average, same conditions
$\sigma_{\text{bio-oil}} = 1.33\%$; $\sigma_{\text{char}} = 0.148\%$

Red oak (0.75 mm)
6 run average, different conditions
$\sigma_{\text{bio-oil}} = 2.21\%$; $\sigma_{\text{char}} = 1.89\%$

*Auger pyrolyzer, ISU (2008)

Efficiency and cost of bio-oil production

- Energy efficiency
  - Conversion to 75 wt-% bio-oil translates to energy efficiency of 70%
  - If carbon used for energy source (process heat or slurried with liquid) then efficiency approaches 94%
- Cost
  - $17-$30/bbl (assuming feedstock cost of $50/ton)

Bio-Oil

- Advantages include:
    - Liquid fuel
    - Decoupled conversion processes
    - Easier to transport than biomass or syngas
- Disadvantages
    - High oxygen and water content makes bio-oil inferior to petroleum-derived fuels
    - Phase-separation and polymerization and corrosiveness make long-term storage difficult

Recovery of Bio-oil as Fractions

Pyrolyzed corn fiber from wet milling

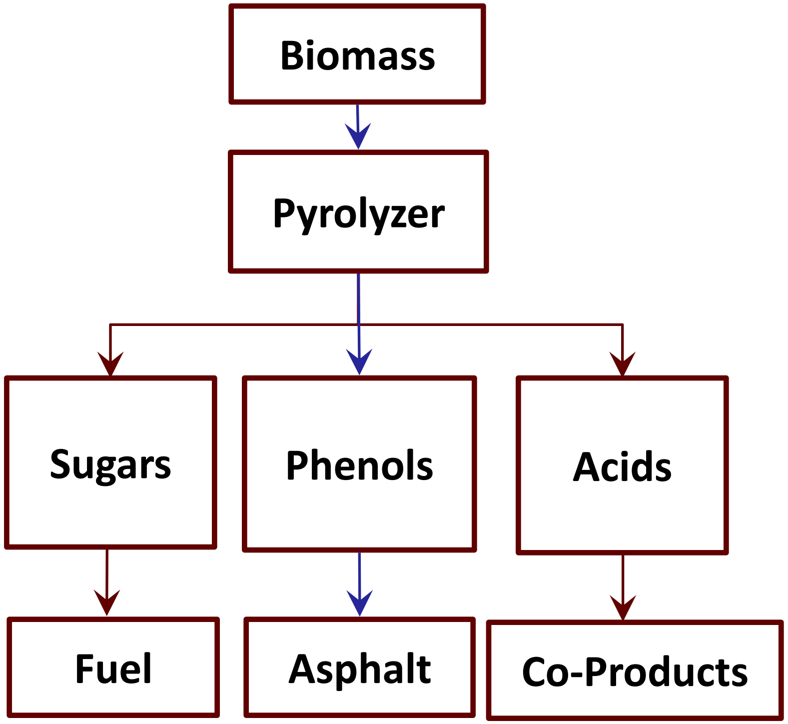
	Fraction 1	Fraction 2	Fraction 3	Fraction 4
Yield (wt-% of biomass)	8.0%	6.0%	29.2%	21.3%
Moisture	1.54%	6.43%	5.63%	74.94%
Major chemicals	levoglucosan	phenolics	lignin oligomers	acids

Characteristics of Bio-oil Fractions

Property	Cond. 1	Cond. 2	Cond. 3	Cond. 4	ESP
Fraction of total oil (wt%)	6	22	37	15	20
pH	-	3.5	2.7	2.5	3.3
Viscosity @40oC (cSt)	Solid	149	2.2	2.6	543
Lignin Content (wt%)	High	32	5.0	2.6	50
Water Content (wt%)	Low	9.3	46	46	3.3
C/H/O Molar Ratio	1/1.2/0.5	1/1.6/0.6	1/2.5/2	1/2.5/1.5	1/1.5/0.5

Products Generated from Bio-Oil

- Biomass pyrolyzed to bio-oil
- Bio-oil fractions converted to renewable fuel, asphalt, and other products



Biomass

Pyrolyzer

Sugars

Phenols

Acids

Fuel

Asphalt

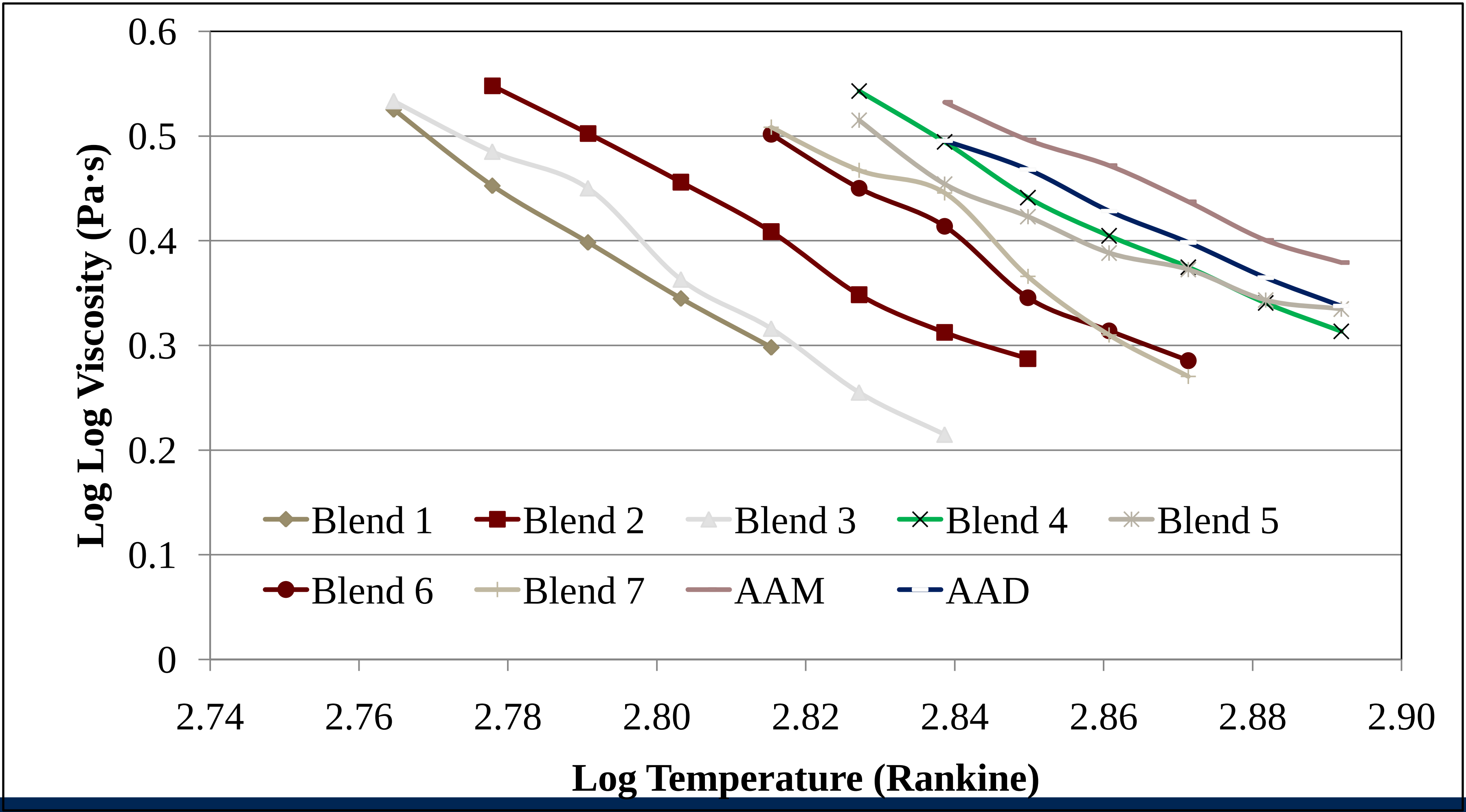
Co-Products

Experimental Plan

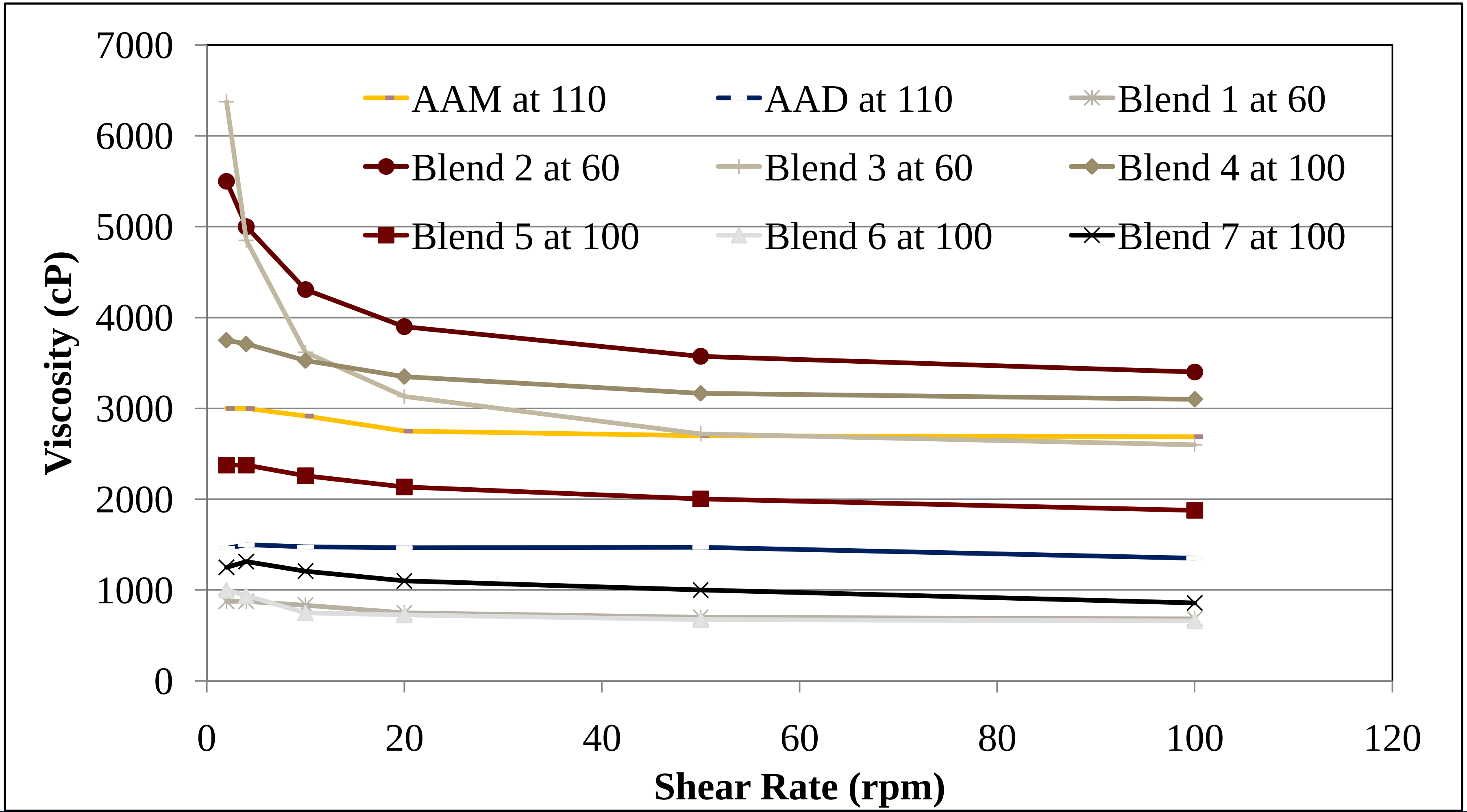
Blend #	Binder Type	Polymer Modifier Type	Blending Percentage
AAM	Bitumen	None	None
AAD			
Blend 1	Oakwood Bio-oil	Control	
Blend 2		P1	2
Blend 3		P1	4
Blend 4		P2	2
Blend 5		P2	4
Blend 6		P3	2
Blend 7		P3	4

Property	**Polyethylene (P1)**	**Oxidized Polyethylene (P2)**	**Polyethylene (P3)**
Drop Point, Mettler (°C)	101	108	115
Density (g/cc)	0.91	0.93	0.93
Viscosity @140°C (cps)	180	250	450
Bulk Density (kg/m^3)	563	536	508

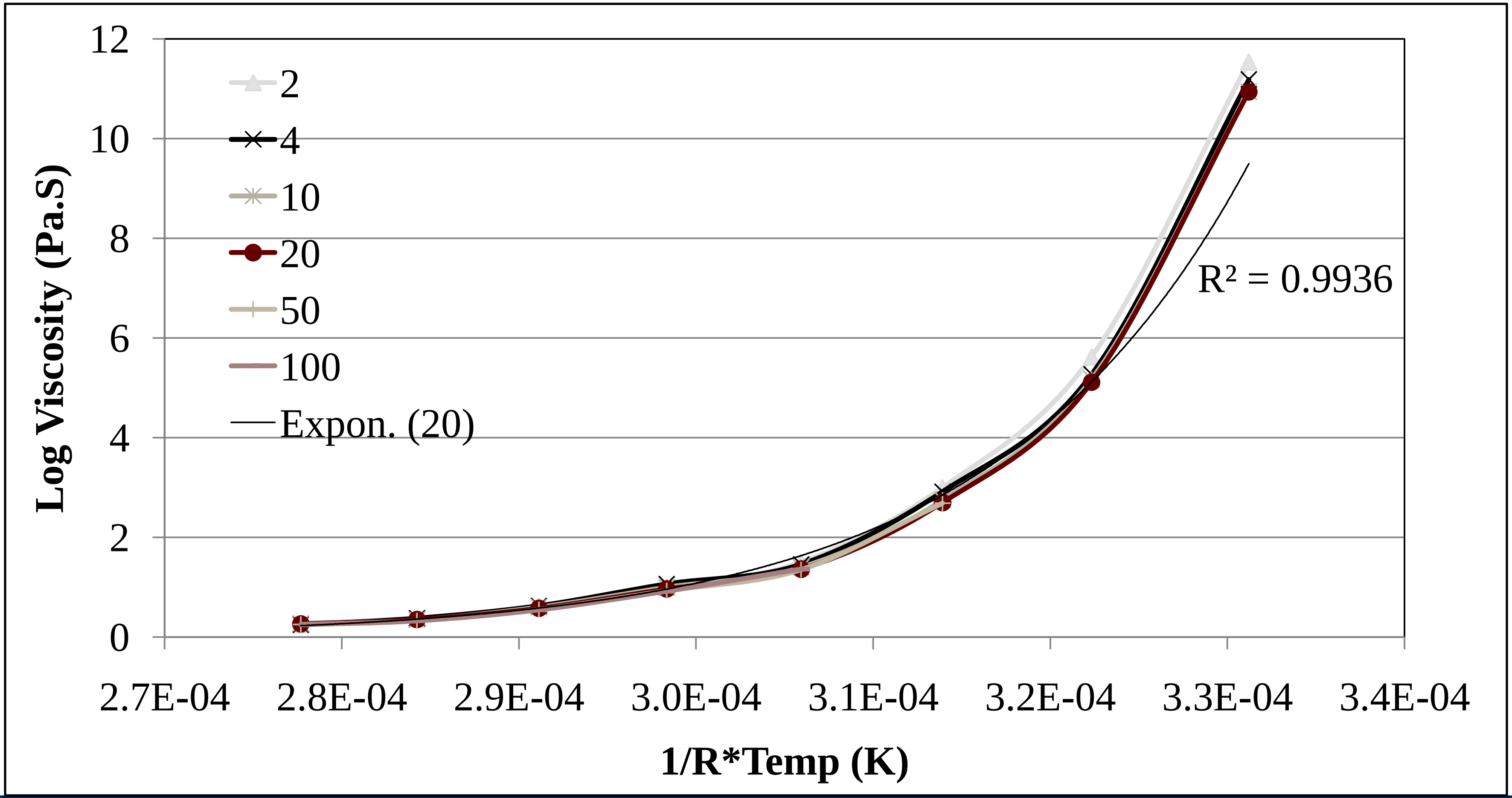
Viscosity-Temperature Susceptibility



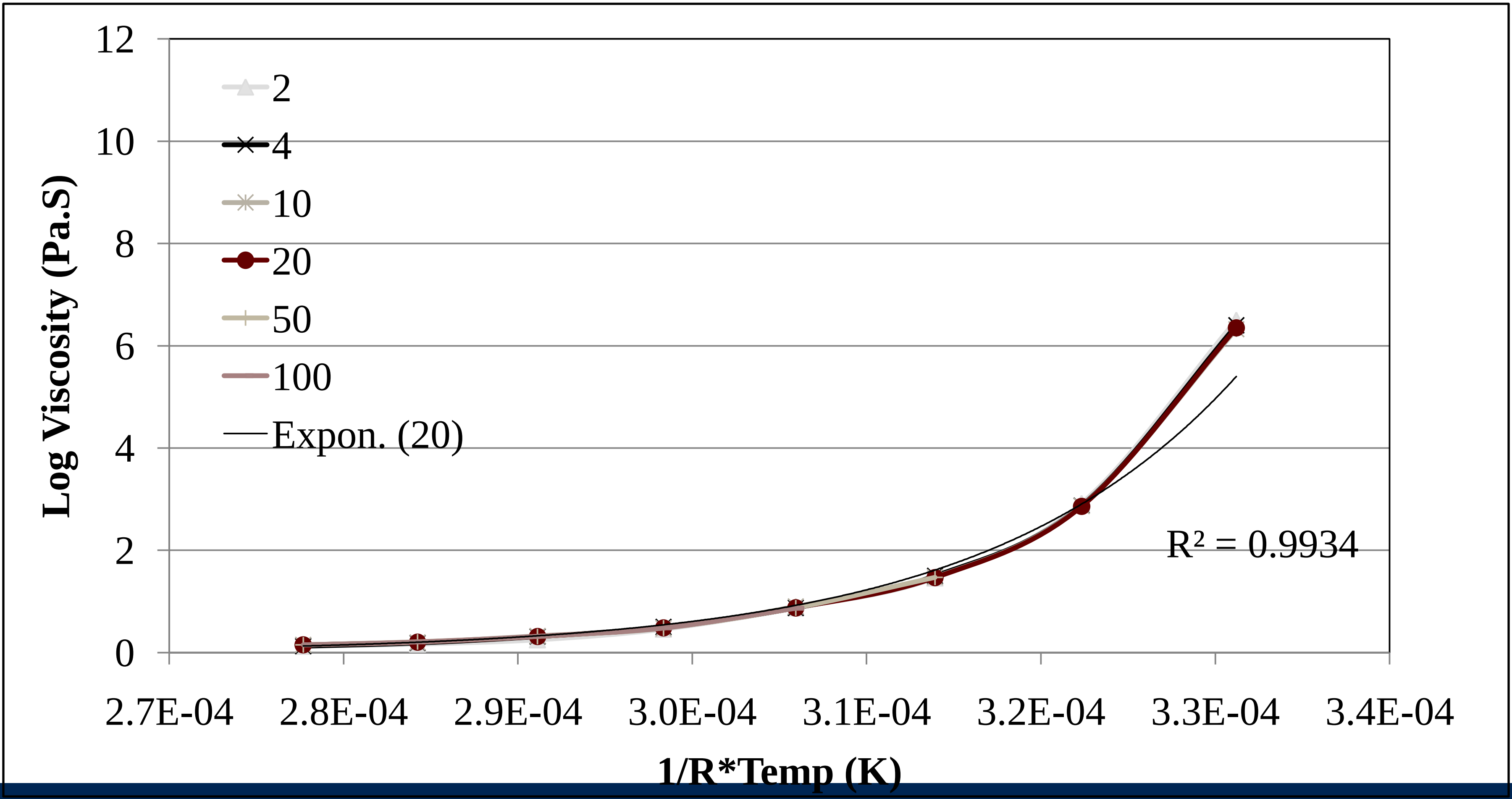
Effect of Shear Rate on Viscosity



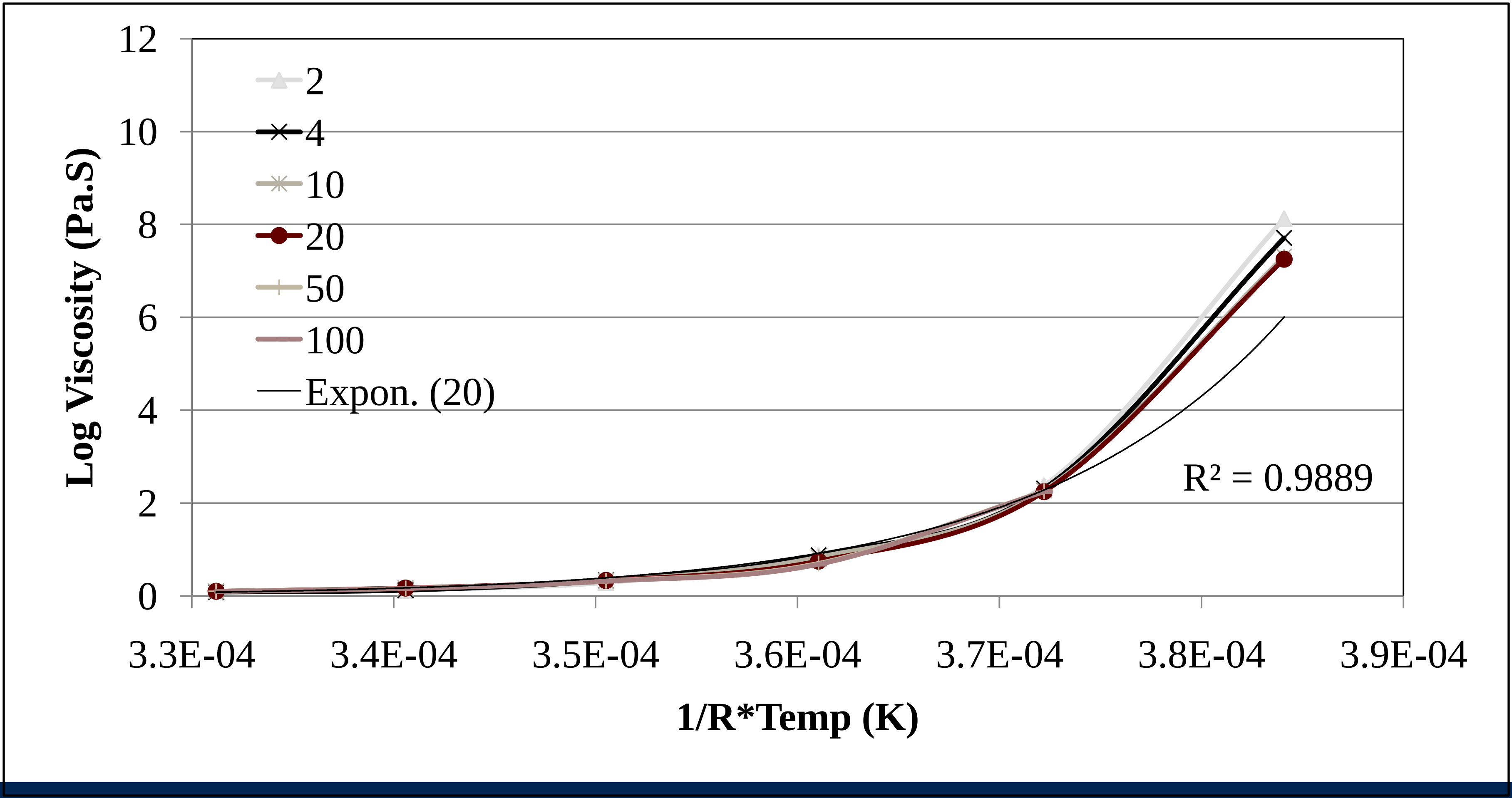
Arrhenius Model for AAM



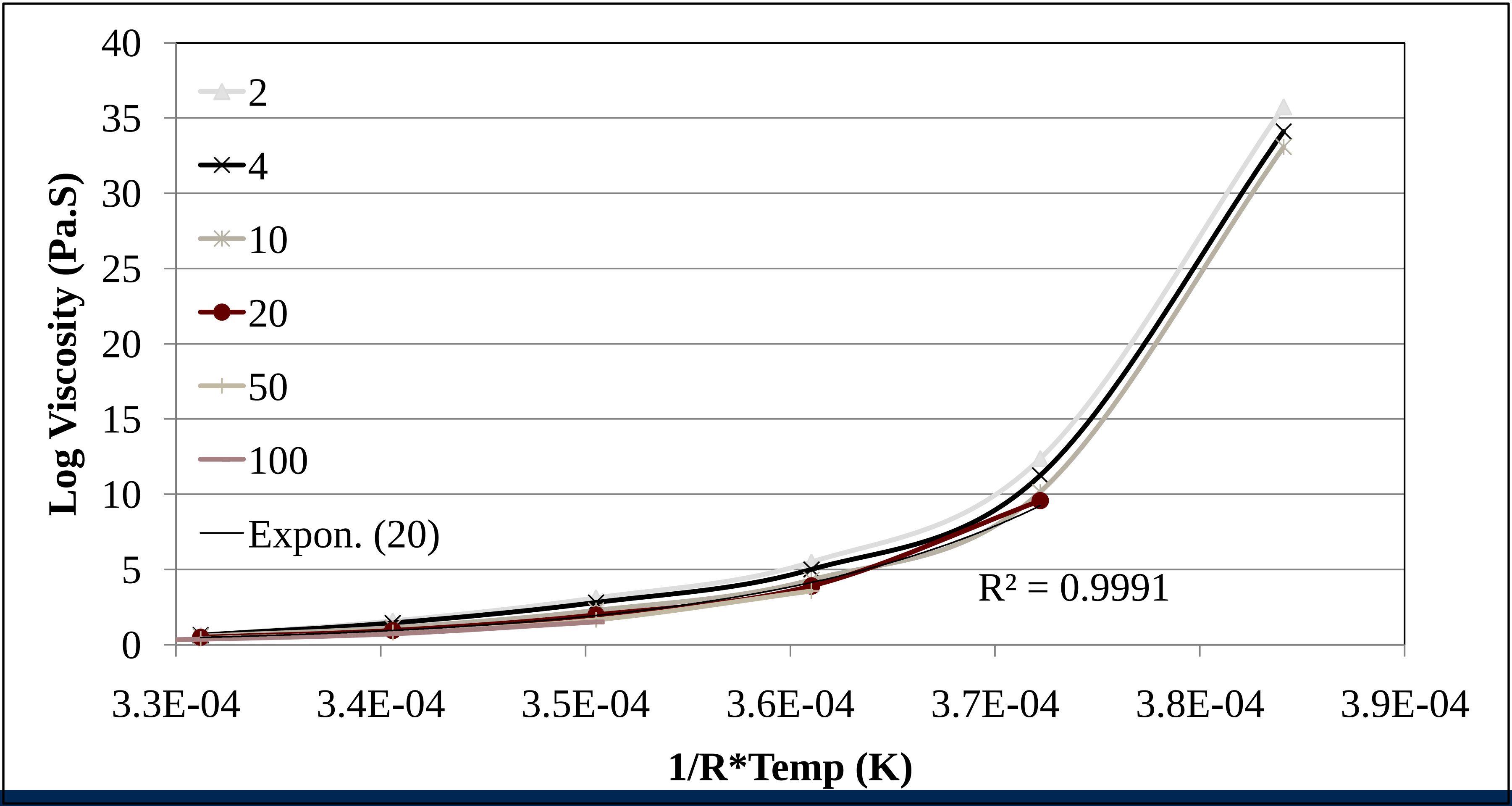
Arrhenius Model for AAD



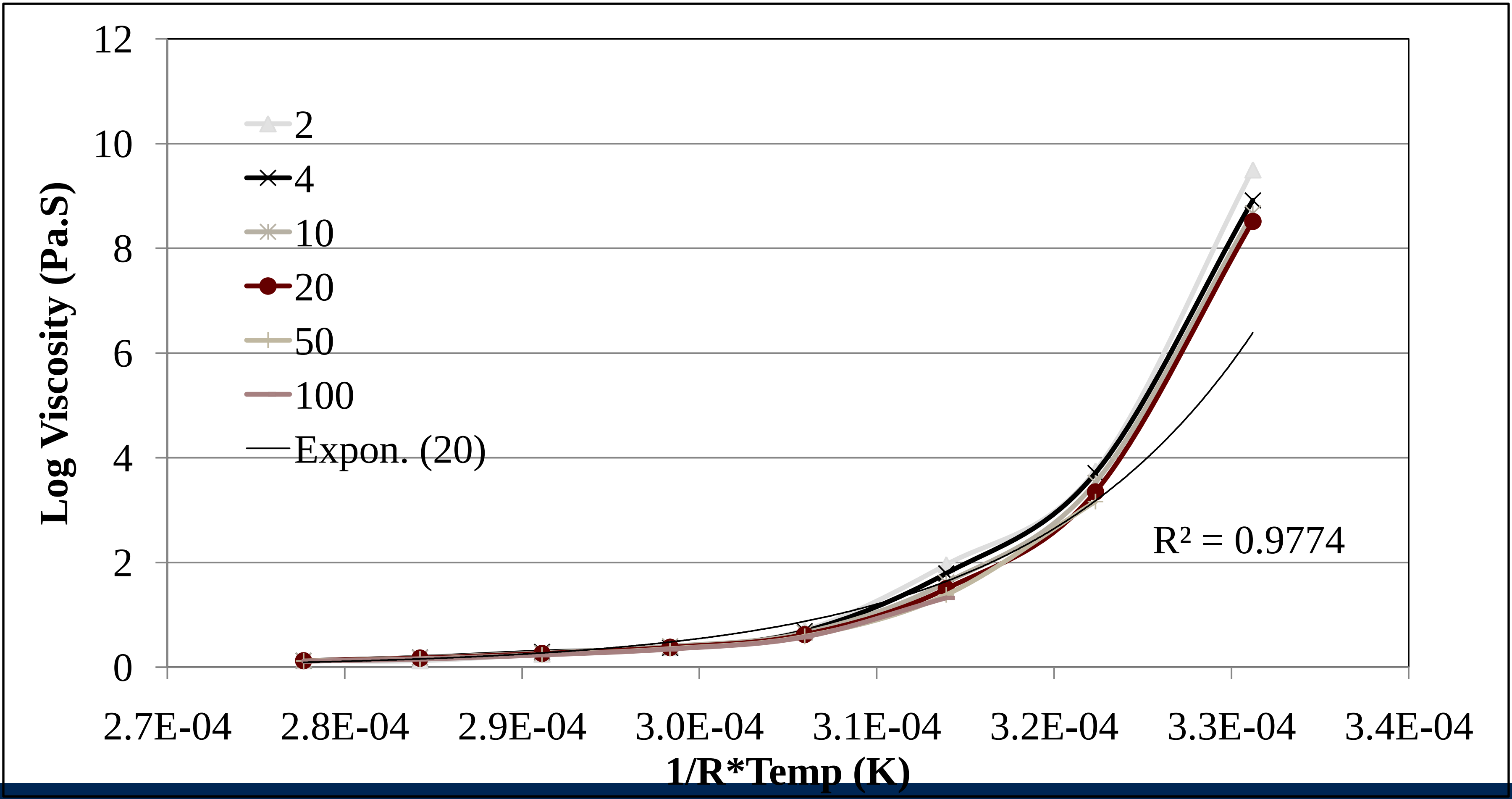
Arrhenius Model for Blend 1



Arrhenius Model for Blend 2



Arrhenius Model for Blend 4



Secondary Charcoal Generation

Bio-char: Soil amendment & carbon sequestration

SEQUESTRATION **NEWS FEATURE** NATURE|Vol 442|10 August 2006

J. LEHMANN

Drop of the black stuff: *terra preta* contrasts strongly with normal soil in colour (left) and produces much more vigorous crops (below).

EPRIDA/UGA BIO-CONVERSION CENTER

Black is the new green

In 1879, the explorer Herbert Smith regaled the readers of *Scribner's Monthly* with tales of the Amazon, covering everything from the tastiness of tapirs to the extraordinary fecundity of the sugar plantations. "The cane-field itself," he wrote of one rum-making operation, "is a splendid sight; the stalks ten feet high in many places, and as big as one's wrist." The secret, he went on, was "the rich *terra preta*, 'black land,' the best on the Amazons. It is a fine, dark loam, a foot, and often two feet thick."

Last month, the heirs to Smith's enthusiasm met in a hotel room in Philadelphia, Pennsylvania, during the World Congress of Soil Science. Their agenda was to take *terra preta* from the annals of history and the backwaters of the Amazon into the twenty-first century world of carbon sequestration and biofuels.

They want to follow what the green revolution did for the developing world's plants with a black revolution for the world's soils. They are aware that this is a tough sell, not least because hardly anyone outside the room has heard of their product. But that does not dissuade them: more than one eye in the room had a distinctly evangelical gleam.

The soil scientists, archaeologists, geographers, agronomists, and anthropologists who study *terra preta* now agree that the Amazon's dark earths, *terra preta do índio*, were made by the river basin's original human residents, who were much more numerous than formerly supposed. The darkest patches correspond to the middens of settlements and are cluttered with crescents of broken pottery. The larger patches were once agricultural areas that the farmers enriched with charred trash of all sorts. Some soils are thought to be 7,000 years old. Compared with the surrounding soil, *terra preta* can contain three times as much phosphorus and nitrogen. And as its colour indicates, it contains far more carbon. In samples taken in Brazil by William Woods, an expert in abandoned settlements at the University of Kansas in Lawrence, the *terra preta* was up to 9% carbon, compared with 0.5% for plain soil from places nearby[1].

From Smith's time onwards, the sparse scholarly discussion of *terra preta* was focused mainly on the question of whether 'savages' could have been so clever as to enhance their land's fertility. But Woods' comprehensive bibliography on the subject now doubles in size every decade. About 40% of the papers it contains were published in the past six years.

Loam ranger

The main stimulus for this interest was the work of Wim Sombroek, who died in 2003 and is still mourned in the field. Sombroek was born in the Netherlands in 1934 and lived through the Dutch famine of 1944 — the *Hongerwinter*. His family kept body and soul together with the help of a small plot of land made rich and dark by generations of laborious fertilization. Sombroek's father improved the land in part by strewing it with the ash and cinders from their home. When, in the 50s, Sombroek came across *terra preta* in the Amazon, it reminded him of that life-giving 'plaggen' soil, and he more or less fell in love. His 1966 book *Amazon Soils* began the scientific study of *terra preta*.

Since then trial after trial with crop after crop has shown how remarkably fertile the *terra preta* is. Bruno Glaser, of the University of Bayreuth, Germany, a sometime collaborator of Sombroek's, estimates that productivity of crops in *terra preta* is twice that of crops grown in nearby soils[2]. But it is easier to measure the effect than explain it through detailed analysis.

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NATURE|Vol 442|10 August 2006 SEQUESTRATION **NEWS FEATURE**

Everyone agrees that the explanation lies in large part with the char (or biochar) that gives the soil its darkness. This char is made when organic matter smoulders in an oxygen-poor environment, rather than burns. The particles of char produced this way are somehow able to gather up nutrients and water that might otherwise be washed down below the reach of roots. They become homes for populations of microorganisms that turn the soil into that spongy, fragrant, dark material that gardeners everywhere love to plunge their hands into. The char is not the only good stuff in *terra preta* — additions such as excrement and bone probably play a role too — but it is the most important factor.

Leaving aside the subtleties of how char particles improve fertility, the sheer amount of carbon they can stash away is phenomenal. In 1992, Sombroek published his first work on the potential of *terra preta* as a tool for carbon sequestration[3]. According to Glaser's research, a hectare of metre-deep *terra preta* can contain 250 tonnes of carbon, as opposed to 100 tonnes in unimproved soils from similar parent material. The extra carbon is not just in the char — it's also in the organic carbon and enhanced bacterial biomass that the char sustains.

Ground control

That difference of 150 tonnes is greater than the amount of carbon in a hectare's worth of plants. That means turning unimproved soil into *terra preta* can store away more carbon than growing a tropical forest from scratch on the same piece of land, before you even start to make use of its enhanced fertility. Johannes Lehmann of Cornell University in Ithaca, New York, has studied with Glaser and worked with Sombroek. He estimates that by the end of this century *terra preta* schemes, in combination with biofuel programmes, could store up to 9.5 billion tonnes of carbon a year — more than is emitted by all today's fossil-fuel use[4].

Mud pack

The year before he died, Sombroek helped to round up like-minded colleagues into the Terra Preta Nova group, which looks at the usefulness of using char in large-scale farming and as a carbon sink. The group was well represented at the Philadelphia meeting, although Glaser was not there. Their aim is to move beyond the small projects in which many of them are involved and find ways of integrating char into agribusiness. After all, wherever there is biomass that farmers want to get rid of and that no one can eat, char is a possibility. That means there are a lot of possibilities.

One problem is that there is a new competitor for farm waste. Plant are largely made up of cellulose, indigestible material in cell walls. Recent technological advances make it likely that quite a lot of that cellulose might be turned into biofuel. At the moment, ethanol is made from corn in the United States and from sugar in Brazil; if it were made directly from cellulose, producers could work with a wider range of cheaper biomass. Given the choice of turning waste material into fuel or into charcoal, farmers might be expected to go for fuel, especially if that is the way that policy-makers are pushing them: US President George W. Bush promised $150 million for work on cellulosic ethanol in his 2006 state of the union speech.

But Lehmann and his colleagues don't see biofuel as an alternative to char — they see the two developing hand in hand. Take the work of Danny Day, the founder of Eprida. This "for-profit social-purpose enterprise" in Athens, Georgia, builds contraptions that farmers can use to turn farm waste into biofuel while making char. Farm waste (or a crop designed for biofuel use) is smouldered — pyrolysed, in the jargon — and this process gives off volatile organic molecules, which can be used as a basis for biodiesel or turned into hydrogen with the help of steam. After the pyrolysation, half of the starting material will be used up and half will be char. That can then be put back on the fields, where it will sequester carbon and help grow the next crop.

Negative thinking

The remarkable thing about this process is that, even after the fuel has been burned, more carbon dioxide is removed from the atmosphere than is put back. Traditional biofuels claim to be 'carbon neutral', because the carbon dioxide assimilated by the growing biomass makes up for the carbon dioxide given off by the burning of the fuel. But as Lehmann points out, systems such as Day's go one step further: "They are the only way to make a fuel that is actually carbon negative".

C. STEINER

Slow burn: the idea of using charcoal to sequester carbon may take a while to catch on.

Day's pilot plant processes 10 to 25 kg of Georgia peanut hulls and pine pellets every hour. From 100 kg of biomass, the group gets 46 kg of carbon — half as char — and around 5 kg of hydrogen, enough to go 500 kilometres in a hydrogen-fuel-cell car (not that there are many around yet). Originally, Day was mostly interested in making biofuel; the char was just something he threw out, or used to make carbon filters. Then he discovered that his employees were reaping the culinary benefits of the enormous turnips that had sprung up on the piles of char lying around at the plant. Combining this char with ammonium bicarbonate, made using steam-recovered hydrogen, creates a soil additive that is now one of his process's selling points; the ammonium bicarbonate is a nitrogen-based fertilizer.

"We don't maximize for hydrogen; we don't maximize for biodiesel; we don't maximize for char," says Day. "By being a little bit inefficient with each, we approximate nature and get a completely efficient cycle." Robert Brown, an engineer at Iowa State University in Ames, has a $1.8-million grant from the United States Department of Agriculture (USDA) to fine-tune similar technology, although being in Iowa, he uses corn stalks not peanut hulls. "We are trying an integrated approach: we are trying to evaluate the agronomic value, the sequestration value, the economic value, the engineering," he says.

Brown thinks a 250-hectare farm on a char-and-ammonium-nitrate system can sequester 1,900 tonnes of carbon a year. A crude calcu-

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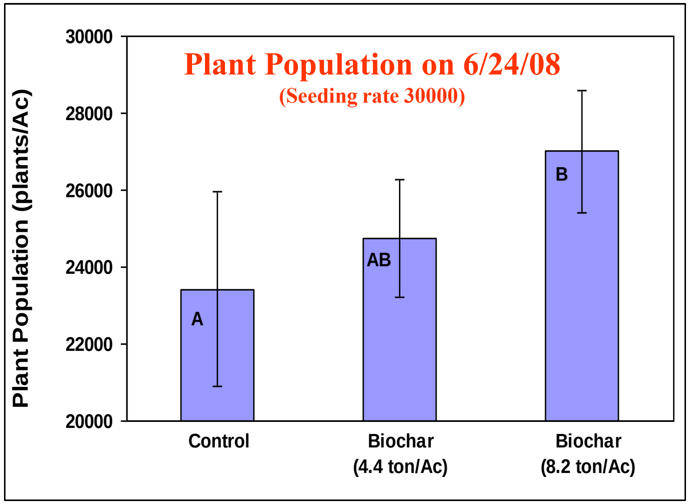
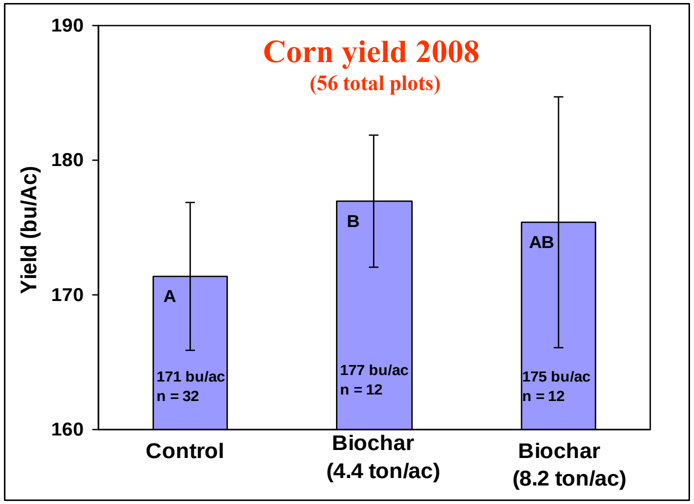
Several studies have reported large increases in crop yields from the use of biochar as a soil amendment. However, most of these studies were conducted in the tropics on low fertility soils. Need to study how temperate region soils will respond to biochar amendments.

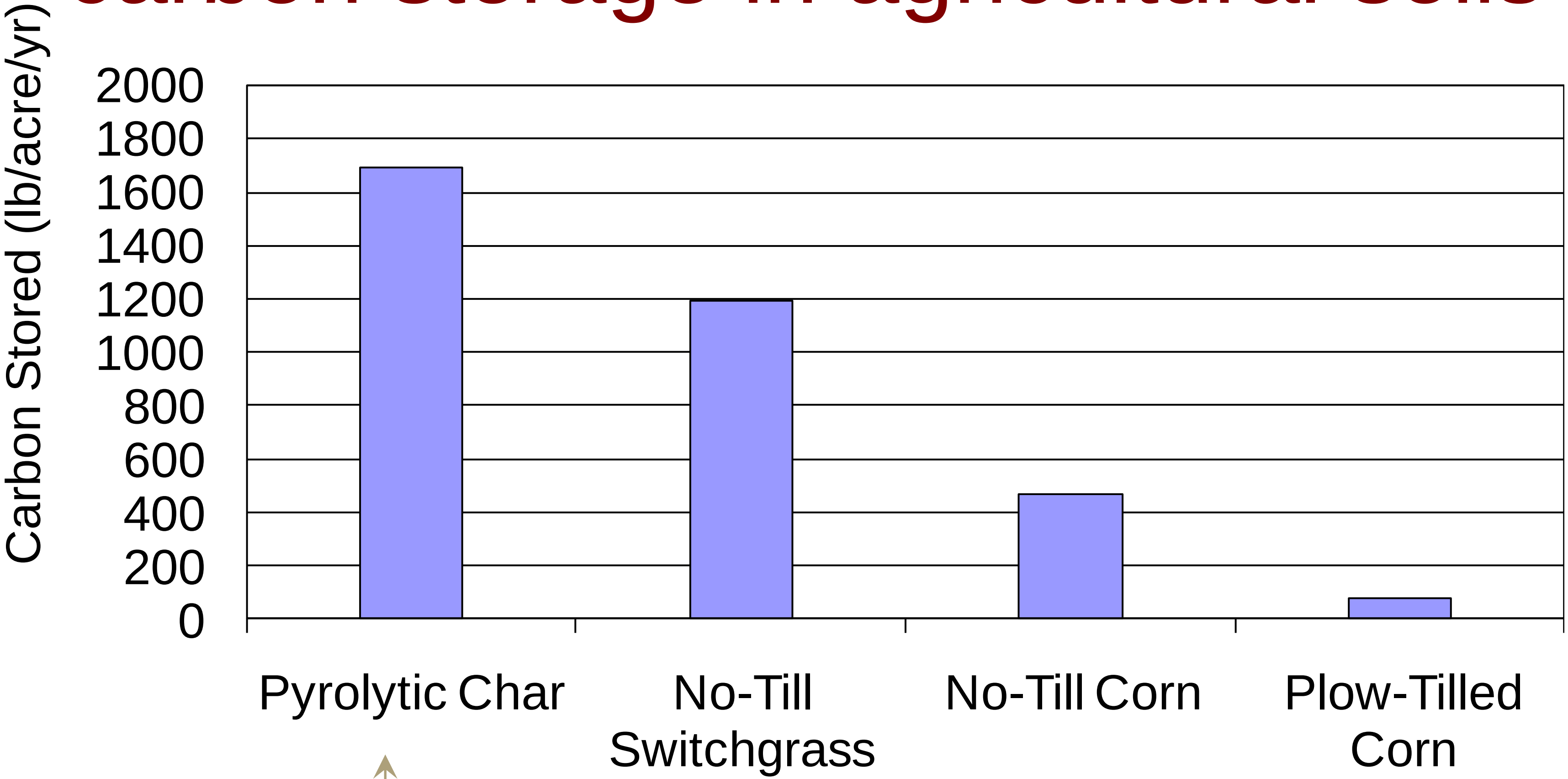


First year trials in Iowa showed a 15% increase plant populations, and a 4% increase in corn grain yield from biochar applications.*



***However, biochar quality is very important. The wrong type of biochar can cause yield decreases!**

Greenhouse gases reduced by carbon storage in agricultural soils



Char from pyrolyzing one-half of corn stover

Summary

- Bio asphalt has similar temperature sensitivity to petroleum derived asphalt.
- The temperature range for the bio-oil and bitumen blends were different.
- An asphalt derived from biomass has been developed that behaves like a viscoelastic material just like petroleum derived asphalt.
- The bio asphalt can be produced locally
- The production process sequesters greenhouse gases.

Ongoing Activities

- Performance grade binders have been developed
- Mix performance testing
  - Rutting
  - Fatigue Cracking
  - Thermal Cracking
- Building test pavement sections

Moving Forward

- Laboratory mix performance
- Scale up of production facilities
  - Substantial capital investment
  - Multiple end markets for pyrolysis products
- Demonstration projects
- Biomass composition varies, and thus products can vary

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Thank You!
&
Questions?