An Integrated, Semi-Automated Approach to Thermochemical Conversion Research for Sustainable Farming Systems

K.B. Cantrell & J.H. Martin II
Coastal Plains Soil, Water, and Plant Research Center
USDA-ARS
Florence, SC, USA
keri.cantrell@ars.usda.gov

Abstract— **An integrated, semi-automated system is presented for the rapid and efficient testing and production of research-scale quantities of biochar. This biochar, produced from agricultural waste materials, can easily be incorporated in future sustainable livestock farming systems. These farming systems will be able to diversify farm income by generating a consistent, predictable, marketable product. Before biochar is incorporated into production systems, it needs to be assessed for its potential to improve soil or crop systems or produce energy. To assess the potential of biochar and proceed quickly from experimental design to experimental results, a variety of analytical instrumentation, control technologies, and processing technologies were brought together to decrease analysis time and double production of a wide variety of biochar types.**

I. INTRODUCTION

Thermochemical conversion (TCC) is a physical conversion of biomass using high temperatures to break the bonds of organic matter and reform these intermediates into synthesis gas, combustible liquid fraction or oil, and/or a solid charred residual termed biochar [1-4]. The volatile gases are a mixture of H_2, CO, CO_2, N_2, water vapor, hydrocarbon gases, and tars. A portion of the volatile gases condense to form a combustible bio-oil; heavier condensable oils can form a tar-like substance. The unreacted, solid residual is a combination of minerals and fixed carbon, commonly referred to as biochar (Fig. 1). In addition to TCC being a mass consumer of a feedstock's organic portion, TCC processing as a means of waste treatment has a number of other benefits: (1) small footprint; (2) efficient nutrient recovery; (3) no fugitive gas emissions; (4) short processing time; (5) capability of handling a variety of feedstocks and heterogeneous blends; and (6) high-temperature elimination of pathogens and pharmaceutically active compounds [2, 5]. Thermochemical conversion processes include combustion, pyrolysis, and gasification. Pyrolysis and gasification have received increasing attention because of their versatility. Whereas gasification is performed at temperatures greater than 800°C under slightly oxidative atmosphere (limited oxygen so as to avoid combustion), pyrolysis is the anoxic breakdown of organic matter occurring at temperatures between 300 and 700°C. Careful process selection from these options -- while considering the availability of feedstock, feedstock characteristics, and the final desired end-product form (i.e., gas, bio-oil, or biochar) -- may yield an economic advantage for agriculture.

Thermochemical conversion based systems have been proposed to treat livestock wastes and convert the organic portion into bioenergy and other value-added products [2, 5, 6]. Utilizing animal wastes in this manner will achieve the following: (1) increase annual revenues; (2) moderate the impacts of commodity prices; and (3) diversify farm income. Concomitantly, this utilization will evolve into new state-of-the-art waste management systems with the added benefit of creating environmentally benign livestock operations [6]. In the case of a pyrolytic-based farming system (Fig. 2), conditioned and dry wastes (e.g., poultry litter or polymer-flocculated, separated swine solids) are pyrolyzed into a combination of combustible gas, bio-oil, and biochar; the combustible gas and bio-oil can be used as a heat source for either the livestock house or the pyrolysis process; the biochar product has an assortment of potential applications: energy production; soil and crop improvement; adsorption of contaminants such as ammonia and greenhouse gases; and carbon sequestration [7].

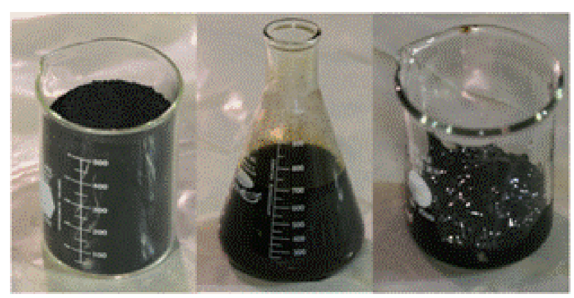

Figure 1. Pyrolysis coproducts: Biochar (left), Bio-oil (middle), and Tar (right)

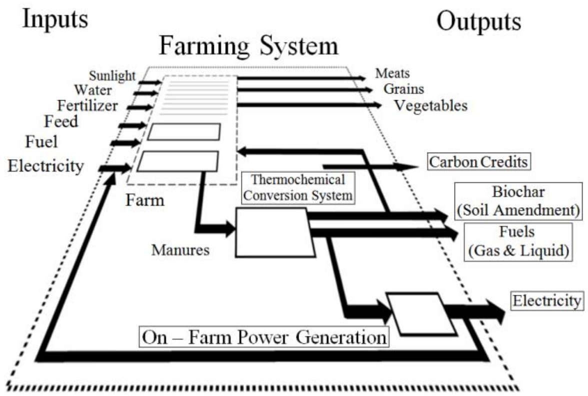

Figure 2. Pyrolytic-based sustainable farming system.

Even with a plethora of uses for the biochar, a critical concern is the generation of a consistent, predictable, and controllable product (1) for research at bench scale and (2) to establish metrics for fair market trade at commercial scale. The objective of this study was to implement a system that analyzed and generated manure-based biochar for research purposes.

II. Systems Used in Research

When animal waste is used to generate biochar, processing and conversion need to overcome waste's heterogeneous nature. Operating parameters during pyrolysis that influence the resultant physicochemical properties of biochar include the following: pressure; heating rate; residence time; highest treatment temperature (HTT); and flow rate of gaseous inputs (e.g., N_2) [8]. In order to better predict the outcome of the pyrolytic process, a rapid analysis of the incoming feedstock and outgoing biochar is needed using software, instrumentation and methodology that can be fully integrated.

Using an integrated experimental approach is more practical than the use of a global theoretical model because of the fuzzy and uncontrollable agrarian variables involved: feedstock composition; livestock housing conditions (e.g., treatment system used and feed rations); regional characteristics such as soil series and soil microbial diversity; irrigation and water supply regimes; etc. Because of these variables, farmers and livestock producers make most agricultural decisions based on either empirical data from regional research or personal experience. Thus, research results need to be related to animal type, plant response and soil fertility. Experiments addressing these topics can quickly become complex (Fig. 3) requiring significant amounts of biochar produced at varied conditions and applied to varied agrarian schemes. To aid in assessments, two highly integrated systems are needed: one system to analyze both feedstocks and biochar; and another to rapidly produce controlled consistent samples of biochar.

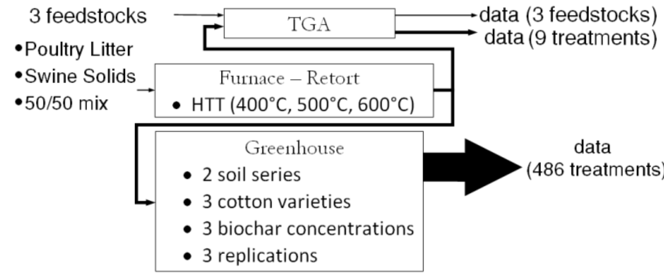

Figure 3. Demonstration of increasing complexity in biochar experiment.

A. Thermogravimetric Analyzer

When testing consistency of feedstocks and biochars, one useful methodology is thermogravimetric analysis. A thermogravimetric analyzer (TGA) records the mass change of a laboratory-scale sample (<5g) exposed to an oxidative or inert carrier gas under a specified temperature profile. Common TGA methods are listed in Table 1. The TGA techniques have been demonstrated using many feedstocks such as food processing residues [9], grasses and straws [10], yard and municipal solid waste [11], and poultry litter [12]. However, as a result of the sophisticated instrumentation and analysis, there are bottlenecks in the final assessments—namely efficiency to generate rapid results.

These devices have been upgraded by manufacturers to include features like auto-samplers and gas switching devices to allow the TGA to perform more work with less human interaction. To further reduce human interaction and gain increased accuracy and speed, custom software and state-of-the-art algorithms can be applied to modularized steps within the entire process. By increasing the role of the software and combining both the speed and the multiplicity of tests a TGA can perform, samples can be quickly characterized with fewer errors allowing for rapid turnover of experiments investigating changes in pyrolytic processing parameters, different feedstocks and blends, and effects of feedstock production treatments on the end products.

B. Furnace-Retort System

Use of the TGA is targeted for purely analytical purposes. Though quick and versatile, the TGA does not generate research-scale quantities of biochar that are necessary for plant response and soil fertility research. Research-scale production can be achieved with a batch system consisting of a retort within a box furnace. While operation of this unit is elementary, the bottleneck to sufficient biochar production is the time required to ensure proper operation of both the heating and cooling stages. In addition, with the scale-up, particular attention must be made to achieve repetitive and consistent procedures. Accordingly, there is a need to bring together controls and processing technologies to maximize production, rapidly implement different processing treatments, and lastly, efficiently analyze the biochar product.

TABLE I. COMMON TGA TEST METHODS

Test	Analysis
10°C/min N_2	Devolatilization (Pyrolysis) Characteristics
10°C/min Air	Combustion Characteristics
Modified ASTM D-3175 [13]	Volatile Matter
Modified ASTM D-3174[13]	Ash (Chars & Manures)
ASTM E 1755	Ash (Plant Biomass)

III. BIOCHAR PRODUCTION WITH AN INTEGRATED, SEMI-AUTOMATED APPROACH

The existing experimental test for biochar production processes is as follows: (1) hypothesis formulation; (2) experimental design; (3) experimental testing (4) result generation; and (5) drawing inferences and conclusions. By integrating steps 2-3 and semi-automating procedures as shown in Fig. 4 (unshaded boxes), it was possible to reduce mistakes, increase speed, and encapsulate parts of the experimental process. Primarily, the parts of the experimental process involving translation from a statistical design to a machine executable process had the best opportunities for automation.

A. Thermogravimetric Analysis

The thermogravimetric experiments used fine ground samples (25µg) placed in reusable 70µl AlO_3 crucibles placed in a TGA/SDTA851e (Mettler Toledo International Inc., Columbus, OH) equipped with the following: microbalance; high temperature furnace (maximum temperature 1600°C); automatic sample robot; GC200 gas controller; and circulating water bath (regulated at 22°C). It was operated from a PC with STARe software v 9.10 software (Mettler Toledo International Inc., Columbus, OH) and capable of simultaneously recording mass loss (TG) and temperature differences between a reference point and sample (differential thermal analysis). The TGA was upgraded and further automated as shown in Fig. 4 by adding software to handle the modularized tasks of experimental set-up and analysis of samples using a consistent protocol.

The TGA's accuracy was improved by increasing the signal to noise ratio from the transducers designed to detect the mass and temperature. Since it would have voided the equipment warranty to alter the TGA to strengthen the signal, efforts were made to reduce the noise. The sources of noise influencing TGA transducers where identified as being physical disturbances involving undesired fluctuations in room pressure and temperature but primarily electrical disturbances caused by HVAC units. Powering off HVAC units was not an option as the room temperature had to be regulated to operate the water bath controlling the TGA reference temperature. Noise was attenuated by implementing the following solutions: TGA location away from building support walls; TGA placement on anti-vibration marble slab; TGA encased in 91 cm x 122 cm x 152 cm rectangular structure (Fig. 5, left); and isolation of the TGA's electrical ground.

1) Performing a TGA Experiment

Despite the ability to program many test methods into the TGA, narrowing the number of methods to the most common listed on a standard form simplified the process. These options were automatically assigned to experimental units in the TGA software using macros (written in BASIC-like AutoIT) decreasing the set-up time from 148 seconds to 15 seconds per test.

For each test an empty crucible (Fig. 5, right) had to be weighed. To more efficiently perform the weigh-in process, macros were used to digitally copy weights to the assigned experimental test —thereby, avoiding human transposition. This overcame another time-related bottleneck, the weighing of an individual crucible, which averaged 200 sec. This avoidance was accomplished by removing the weighing of crucibles from integrated work flow as shown in Fig 4 and allowing weighing to be done in parallel with any of the preceding steps.

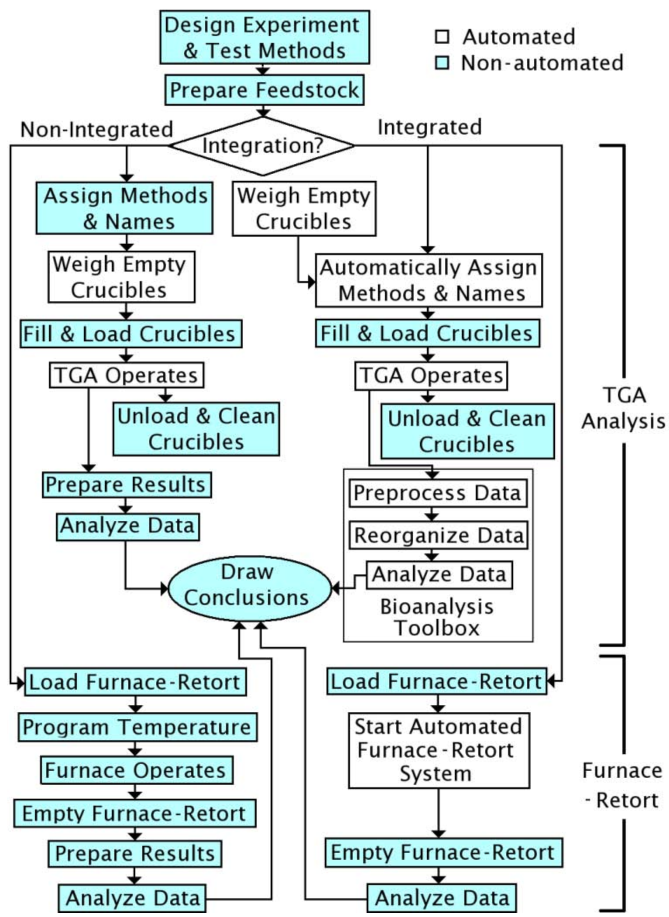

Figure 4. Comparison of non-integrated and integrated TGA assessment and furnace-retort production of biochar.

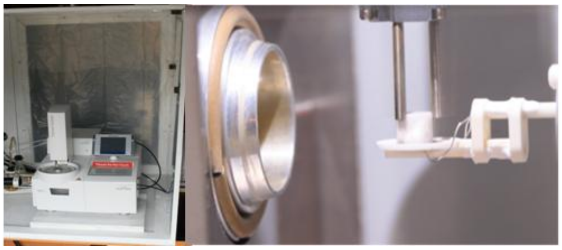

Figure 5. Images of TGA (left)and sample robot loading crucible (right).

No matter what protocol was performed, the software was able to provide consistency. A drying protocol was implemented as detailed in [13] that eliminated both air dry and residual sample moistures that are subject to variations dependent on sample preparation and laboratory humidity. By adding this drying protocol, downstream calculations were avoided that had to adjust composition results (e.g., wt% of ash) from an as-received basis to a dry weight basis—thus, saving time in final presentation of results. Another entry by this software was a high temperature blank crucible run to serve as a mid-queue cleaning after a volatilization test. The effect of this was to burn off any tars that may have volatilized and re-condensed on the TGA arm.

2) Analyzing TGA Data: Bioanalysis Toolbox

For analysis of data, a Bioanalysis Toolbox (Fig. 4) was custom designed and comprised of the following: a preprocessor; data reorganizer; and analysis package. The preprocessing software was developed to use a unique filter that combined existing derivative curve smoothing algorithms and a phase space despiking algorithm [14, 15]. The filter was designed to remove pronounced effects that small perturbations in mass would have on the derivative of the mass curve (DTG). This unique filter removed spikes and made data relevant to the reaction more apparent (Preprocess Data; Fig. 4). This same algorithm was used to reduce the resolution so each graph had 500 points; that number of points was sufficient to plot data and generate graphs that could be quickly and easily manipulated in common spreadsheet programs.

After the data from the TGA was preprocessed, another program was used to convert the data from linear testing sequence to factorial or treatment sequence (Reorganize Data; Fig. 4). Another code was used to aid in the analysis of the data (Analyze Data; Fig. 4). This analysis package performed three primary functions: (1) examine individual curves to verify data integrity; (2) export summarized data to a common spreadsheet program; and (3) generate publishable quality graphs (Fig. 6). Basic analysis of the feedstock using the TGA information could include the following: ash content; volatile matter content; pyrolysis and combustion onset temperature; maximum reaction temperature; and completed reaction temperature. This information aided in determination of the temperature profile for the furnace-retort system including the HTT.

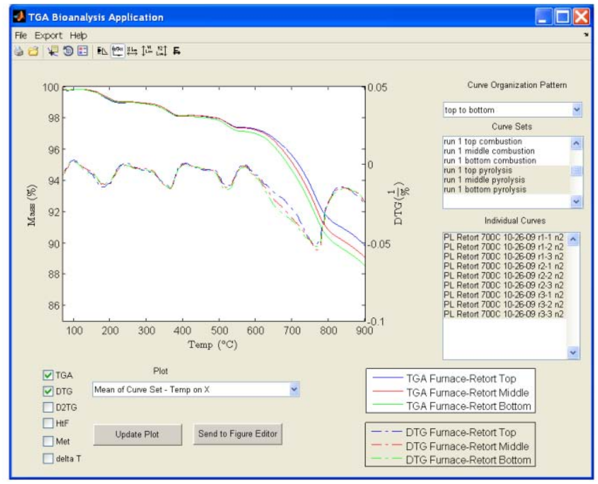

Figure 6. Graphical user interface of TGA Bioanalysis Application.

B. Batch Production of Biochar at Research-scale

To use a fully integrated approach for research-scale production of biochar, the furnace-retort system was designed to operate in a similar manner to the TGA; this was accomplished to directly compare analytical data between the two instruments. The primary difference between the two was the amount of processed feedstock per run; the furnace-retort system had a greater loading capacity than the TGA by a factor of $1x10^5$. The furnace-retort system was comprised of a Signal Lindberg 51662-HR furnace with an internal retort and Eurotherm 2416 controller (Fig. 7). The interior working volume was equipped with an in-house designed loading rack. This loading rack allowed for two improvements in the biochar production: (1) maximize use of working volume with multiple stainless steel trays and (2) quicker sample turnover since trays could be removed with an aluminum peel at up to 200°C temperatures. Bio-oil and gas collection occurred by allowing the exhaust gas to pass through a condenser consisting of Erlenmeyer flasks and copper tubing and vented to the outside air. As described, the system was under manual operation and observation with respect to temperature programs and gas flow control.

The system and biochar production procedures were later semi-automated with the installation of a changeover regulator, mass flow controllers, and National Instruments CompactRIO programmable automation controller (PAC). This system could control the influent gas flow dynamically. The PAC also allowed for gas switching. Gas switching could be used at the end to flush the system with air so as to avoid potential health hazards or in a similar manner as the TGA switching within experimental runs. With appropriate temperature modules, the PAC also had ability to control and record different temperature profiles and the ability to record temperatures at multiple points throughout the process. Semi-automation allowed for labor-free late evening and overnight operation to mitigate odor concerns.

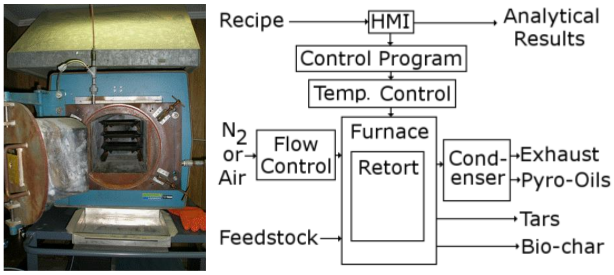

Figure 7. Furnace-retort system with tray system used in biochar production. (left) and system process flow diagram (right).

Biochar from this system was analyzed by the TGA in a similar manner to the feedstock analysis (graphic inset; Fig. 6). This analysis was performed to test the furnace-retort system's ability to generate a consistent product with respect to spatial interior placement (e.g., top tray versus bottom tray). As seen in the graphic inset, initial testing of the semi-automated system produced a biochar with similar volatile matter losses (as noted by the final Mass % ±1%). However, small variations in the DTG curves between 600-800°C suggests potential differences in the biochar's surface chemistry and related functional groups. If biochar were aimed at improving soil fertility, further assessments would be needed to address the stability of the biochar and its response to slow chemical and microbial decompositions.

IV. CONCLUSION

In order to diversify income, future sustainable livestock farming systems will need to implement innovative treatment technologies that convert waste materials into sustainable, marketable products. One option is to use pyrolysis, where farming systems will be able to generate biochar that has a multitude uses including energy production, carbon sequestration, and soil and crop improvement. With biochar's agronomic properties easily affected by processing conditions, it is important to assess potential effects on soil and crop response before the biochar enters the production system. Therefore, sufficient quantities of biochar need to be produced for greenhouse research. This research can only grow in complexity involving many treatments. Therefore, the need arises to implement analytical instrumentation and processing technologies that can efficiently assess and generate the needed biochar.

The integrated, semi-automated system presented here made use of a thermogravimetric analyzer (TGA) for rapid analysis of samples and a batch furnace-retort system for research-scale biochar production. Once steps amenable to automation were identified, software was created that was rapidly able to filter, organize, and combine TGA outputs. The results from these outputs could be quickly summarized for scientific presentations. For the furnace-retort system, a programmable automation controller was added to control and record temperatures at multiple points. This addition allowed for the generation of a consistent product. The integrated, semi-automated system provided the ability to overcome bottlenecks thereby maximizing production, reducing operator error, and decreasing analysis time. The TGA portion of the system can be used in various simple or complex experimental designs for routine assessment of feedstocks and conversion products efficiently and conveniently.

ACKNOWLEDGEMENT

Mention of a trade name, proprietary product, or vendor is for information only and does not guarantee or warrant the product by the USDA and does not imply its approval to the exclusion of other products or vendors that may also be suitable.

REFERENCES

[1] A.V. Bridgwater, "Renewable fuels and chemicals by thermal processing of biomass," Chem. Eng. J., vol. 91(2-3), pp. 87-102, 2003.

[2] K. Cantrell, K. Ro, D. Mahajan, M. Anjom, and P.G. Hunt, "Role of thermochemical conversion in livestock waste-to-energy treatments: Obstacles and opportunities," Ind. Eng. Chem. Res., vol. 46(26), pp. 8918-8927, 2007.

[3] P. McKendry, "Energy production from biomass (part 2): Conversion technologies," Bioresour. Technol., vol. 83(1), pp. 47-54, 2002.

[4] P. McKendry, "Energy production from biomass (part 1): Overview of biomass," Bioresour. Technol., vol. 83(1), pp. 37-46, 2002.

[5] K.S. Ro, K. Cantrell, D. Elliott, and P.G. Hunt, "Catalytic wet gasification of municipal and animal wastes," Ind. Eng. Chem. Res., vol. 46(26), pp. 8839-8845, 2007.

[6] K.B. Cantrell, T. Ducey, K.S. Ro, and P.G. Hunt, "Livestock waste-to-bioenergy generation opportunities," Bioresour. Technol., vol. 99(17), pp. 7941-7953, 2008.

[7] J. Lehmann and S. Joseph, "Biochar for Environmental Management: An Introduction," in Biochar for Environmental Management: Science and Technology, J. Lehmann and S. Joseph, Eds. Sterling, VA: Earthscan, 2009, pp. 1-12.

[8] A. Downie, A. Crosky, and P. Munroe, "Physical Properties of Biochar," in Biochar for Environmental Management: Science and Technology, J. Lehmann and S. Joseph, Eds. Sterling, VA: Earthscan, 2009, pp. 13-32.

[9] E. Biagini, F. Barontini, and L. Tognotti, "Devolatilization of biomass fuels and biomass components studied by TG/FTIR technique," Ind. Eng. Chem. Res., vol. 45(13), pp. 4486-4493, 2006.

[10] T.G. Bridgeman, L.I. Darvell, J.M. Jones, P.T. Williams, R. Fahmi, A.V. Bridgwater, et al., "Influence of particle size on the analytical and chemical properties of two energy crops," Fuel, vol. 86(1-2), pp. 60-72, 2007.

[11] E. Smidt and P. Lechner, "Study on the degradation and stabilization of organic matter in waste by means of thermal analyses," Thermochim. Acta, vol. 438(1-2), pp. 22-28, 2005.

[12] N. Whitely, R. Ozao, Y. Cao, and W.P. Pan, "Multi-utilization of chicken litter as a biomass source. Part II. Pyrolysis," Energ. Fuel., vol. 20(6), pp. 2666-2671, 2006.

[13] K.B. Cantrell, J.H. Martin II, and K.S. Ro, "Application of Thermogravimetric Analysis for the Proximate Analysis of Livestock Wastes," Journal of ASTM International, vol. In Review, pp., 2009.

[14] D.G. Goring and V.I. Nikora, "Despiking acoustic doppler velocimeter data," J. Hydra. Eng., vol. 128(1), pp. 117-126, 2002.

[15] K. Wang, S. Wang, H. Huang, M.T. Klein, and W.H. Calkins, "A novel smoothing routine for the data processing in thermogravimetric analysis," ACS Division of Fuel Chemistry, Preprints, vol. 41(1), pp. 27-30, 1996.