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# Co-Production of Chemical and Energy Products from Distillers Grains using Supercritical Fluid Extraction and Thermochemical Conversion Technologies

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## **Co-Production of Chemical and Energy Products from Distillers Grains using Supercritical Fluid Extraction and Thermochemical Conversion Technologies**

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**Abstract.** *Dry-grind technology has become the dominant method for ethanol production. During dry-grind ethanol production, roughly one-third of the dry grain mass resides in the dried distillers grains with solubles (DDGS) as by-products (i.e., ~0.8 kg/L ethanol). The energy content residing in the 0.8 kg DDGS is about 20 MJ, compared to the consumption of 1 MJ electricity and 10 MJ thermal energy for production of each liter of ethanol. A sequential supercritical fluid process with solvents including carbon dioxide, water and ethanol was used to recover high-value chemicals from DDGS. Thermochemical conversion methods were used to convert the DDGS residue after extraction to gaseous and liquid fuels.*

**Keywords.** DDGS, biomass, supercritical fluid processing, thermochemical conversion, gasification, extraction, liquefaction

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## Introduction

Ethanol production continues to expand in the United States. Approximately two-thirds of the current ethanol production capacity is based on dry-grinding technology. Nearly all of the fuel ethanol currently produced in the United States uses corn as a feedstock. During dry-grind ethanol production, approximately one-third of the mass of grain feedstock (i.e., ~0.8 kg/L) resides in the dried distillers grains with solubles (DDGS) as by-products. DDGS are composed of 30-35% crude protein, 40-45% carbohydrates and 15-20% extractives by dry basis (Tucker et al., 2004). The extractives are mainly lipid materials, which can be extracted and refined to high-value nutraceuticals such as policosanols, phytosterols and free fatty acids (Singh et al., 2003; Wang et al., 2005; Wang et al., 2007). The carbohydrates include 10-15% nonstarch glucan, 10-15% xylan, 5-10% arabinan and 5-10% starch, which can be extracted for additional fuel alcohol production (Tucker et al., 2004). For dry-grind production of each liter ethanol, the energy content residing in the 0.8 kg DDGS is about 20 MJ, compared to the consumption of ~0.3 kWh (or 1 MJ) electricity and 10 MJ thermal energy (Eggeman and Verser, 2006). The use of fossil fuels in an ethanol plant not only decreases the sustainability credit of the ethanol industry but also increases its financial risk due to the soaring price of fossil fuels. Thus, DDGS is a potential renewable resource for production of high-value chemicals, and heat and power to an ethanol plant.

Extraction techniques have been investigated widely to obtain valuable natural compounds such as lipids, phytochemicals, pharmaceuticals, flavors, fragrances and pigments from plants (Wang and Weller, 2006). Traditional methods, such as solid-solvent extraction, which have been used for many decades, are very time-consuming and require relatively large quantities of solvents (Luque de Castro and Garcia-Ayuso, 1998). Lipids from plant sources usually are extracted using organic solvents such as n-hexane. The EPA is pushing the industry to develop a viable non-hexane substitute for biomass oil extraction. There is an increasing demand for new extraction techniques with shortened extraction time, reduced organic solvent consumption, and increased pollution prevention (Wang and Weller, 2006). Supercritical fluids are excellent solvents for dissolving organics and biological molecules from biomass. Thus, it is possible to use a series of supercritical fluids to dissolve high-value chemicals from DDGS. A fluid becomes supercritical after it passes its vapor-liquid critical point. A supercritical fluid has both gaseous properties such as high diffusivity, low viscosity and high compressibility, and liquid properties such as high density. The unique properties of supercritical fluids can enhance heat and mass transfer, reaction kinetics and equilibrium between solid biomass and supercritical fluids. Furthermore, due to the high compressibility of supercritical fluids, their solvent properties can be easily adjusted by changing the pressure and temperature. Thus, the products can be recovered easily from the fluids by the reduction of the dissolving power (Wang and Weller, 2006). Supercritical CO<sub>2</sub> (critical point: 73 MPa and 31°C) is an attractive alternative to organic solvents for extraction of high-value non-polar chemicals from plant materials because it is nonexplosive, nontoxic and cheap, and it can be removed easily from the final products (Wang and Weller, 2006). Water (critical point: 21.8 MPa and 374°C), at near- or super- critical conditions, and supercritical ethanol (critical point: 6.1 MPa and 241°C) can liquefy biomass into bio-oil, which can be further refined to sugars, organic acids and other valuable products (Saka, 2006).

Thermochemical conversion provides another competitive way to produce chemical and energy products from low-value and highly distributed biomass resources with large variations in properties (Caputo et al., 2005). Combustion, pyrolysis and gasification are three main thermochemical conversion methods. Biomass pyrolysis converts solid biomass to bio-oil in the absence of an oxidizing agent. Biomass combustion converts biomass into CO<sub>2</sub> and H<sub>2</sub>O and

while generating heat by fully oxidizing the biomass. Biomass gasification converts biomass into a gaseous mixture of syngas consisting of  $H_2$ ,  $CO$ ,  $CH_4$  and  $CO_2$  by partially oxidizing biomass (Demirbas 2004; Yoshioka et al., 2005).

The objective of the research reported herewith was to recover high-value chemicals from DDGS using supercritical fluids including supercritical  $CO_2$ , super or sub-critical water and supercritical ethanol, and further convert the DDGS residue, after extraction, to gaseous and liquid fuels using thermochemical conversion methods.

## Materials and Methods

### *DDGS and reagents*

Corn DDGS were obtained from a local ethanol production facility in Nebraska. Particle size was calculated from the weight and the average particle size of each fraction obtained using a sieve shaker (Ro-TAP, W.S. Tyler, Cleveland, Ohio) equipped with six sieves (U.S. standard sieve Nos. 12, 14, 16, 20, 35 and 140) and a pan. The moisture content of DDGS before and after extraction of their lipids were measured using a moisture analyzer (HG 53 moisture analyzer, Mettler-Toledo GmbH, Laboratory and Weighing Technologies, Greifensee, Switzerland) at a chamber temperature of  $105^\circ C$  (Wang et al., 2005). The heating value of DDGS and their residues after processing were determined using an oxygen bomb calorimeter (Parr Instrument Company, Moline, IL). The density of samples was calculated by dividing the mass of a sample by the sample volume.

### *Supercritical fluid processing of DDGS*

Supercritical fluid processes were carried out in a lab-scale unit equipped with a 300 ml high-pressure processing vessel as shown in Fig. 1.



Fig. 1. Supercritical fluid processing unit.

Temperature of the processing vessel was maintained using a heating tape with a maximum temperature output of 760°C (Extreme-Temperature Heat Tape, McMaster, Atlanta, GA) wrapped around the vessel and regulated with a temperature controller. Pressure was measured using a pressure transducer (Model: PT 420A, Dynisco LLC, Franklin, MA). Temperature was measured using a J-type thermocouple (Newport Scientific, Inc, Jessup, MD). The yield of extract (weight of extracted materials per original weight of DDGS particles) was determined through weight difference of DDGS particles in the processing vessel before and after extraction.

For supercritical CO<sub>2</sub> extraction of lipids, raw DDGS were fed into the supercritical fluid processing vessel. Liquid CO<sub>2</sub> was pumped into the processing vessel with a high-pressure pump (Model 46-1341102, Newport Scientific Inc., Jessup, MD) at a set pressure and flow rate. The lipid compounds in the DDGS were dissolved into the supercritical CO<sub>2</sub>. The mixture of lipids and CO<sub>2</sub> was transferred into the lipid separator, where the pressure of CO<sub>2</sub> was decreased to evaporate the CO<sub>2</sub> from the lipids. The exit fluid of CO<sub>2</sub> from the separator was expanded to ambient pressure through a flow meter (Series 10A3500, Fischer and Porter, Warminster PA) and a gas totalizer (Singer Model DTM-200, Singer American Meter Division, Philadelphia, PA). The flow meter, calibrated in standard liters per hour of CO<sub>2</sub>, was used to determine average flow rates through the extraction system. The gas totalizer was used to measure the total volume of the CO<sub>2</sub> that passed through the extraction system over time.

For sub-critical water processing, a given amount of water and DDGS residue remaining, after supercritical CO<sub>2</sub> extraction, were placed into the high-pressure processing vessel. The temperature of the mixture of DDGS residue and water was increased to 225°C at a heating rate of 5°C/min and the pressure was increased to 24 MPa. The temperature was maintained at the set value for 30 min and then decreased to ambient for about 1 hour. Meanwhile, the pressure was released. After processing, the mixture was filtered through two No. 2 filtration papers. The solid residue was washed using distilled water and the wash water was added into filtrate solution. The solid residue was dried in a vacuum oven at 60°C. The weight of the dried residue was measured at the end of drying. The extract-water solution was concentrated using a vacuum evaporator at 60°C for further composition analysis.

For supercritical ethanol processing, a given amount of ethanol and DDGS residue remaining, after supercritical CO<sub>2</sub> and sub-critical water extraction, were placed into the high-pressure processing vessel. The temperature of the mixture of DDGS residue and water was increased to 250°C at a heating rate of 5°C/min and the pressure was increased to 10 MPa. The temperature was maintained at the set value for 30 min and then decreased to ambient for about 1 hour. Meanwhile, the pressure was released. The mixture after processing was filtered through two No. 2 filtration papers. The solid residue was washed using ethanol and the washing ethanol was added to the filtrate solution. The solid residue was dried in a vacuum oven at 60°C. The weight of the dried residue was measured at the end of drying. The extract-ethanol solution was concentrated using a vacuum evaporator at 40°C for further composition analysis.

### ***Thermal degradation of DDGS residue in nitrogen and air***

The DDGS residue was thermally degraded in a thermogravimetric analyzer (Perkin-Elmer TGA 7, Norwalk, CT). Approximately 15-25 mg of DDGS residue, after extraction of lipids, was placed in the microbalance of the thermogravimetric analyzer for each analysis. Nitrogen and air were used as the purging gases for pyrolysis and combustion analyses, respectively. The flow rate of purging gas was set at 20 ml/min. The temperatures of DDGS samples were increased from the ambient temperature of 20°C to 650°C for the pyrolysis analysis and from 20°C to

850°C for the combustion analysis. The heating rate was set at 30°C/min. Dynamic residual weight of DGS and temperature were recorded and analyzed by a computer using TGA7 software. The TAG data were used to determine the initial degradation temperature of pyrolysis and combustion, degradation rate, residual weight at the end of degradation and kinetic parameters.

## Results and Discussion

### *Super- or sub-critical fluid processing of DDGS*

The yields of supercritical CO<sub>2</sub> solubles, sub-critical water solubles, supercritical ethanol solubles and undissolved solid residue are given in Fig. 2. It can be seen from Fig. 2 that 12.8%, 53.1% and 13.6% of the raw materials, on wet basis, were dissolved in supercritical CO<sub>2</sub> (extraction temperature of 70°C, extraction pressure of 27.5 MPa, mass ratio of solvent to solids of 45, extraction time of 4 hr), sub-critical water (extraction temperature of 225°C, extraction pressure of 24 MPa, mass ratio of water to solids of 5, extraction time of 30 min) and supercritical ethanol (extraction temperature of 250°C, extraction pressure of 10 MPa, mass ratio of ethanol to solids of 5, extraction time of 30 min), respectively. Only about 20.5% of raw DDGS mass was undissolved by the three solvents under the given operating conditions.

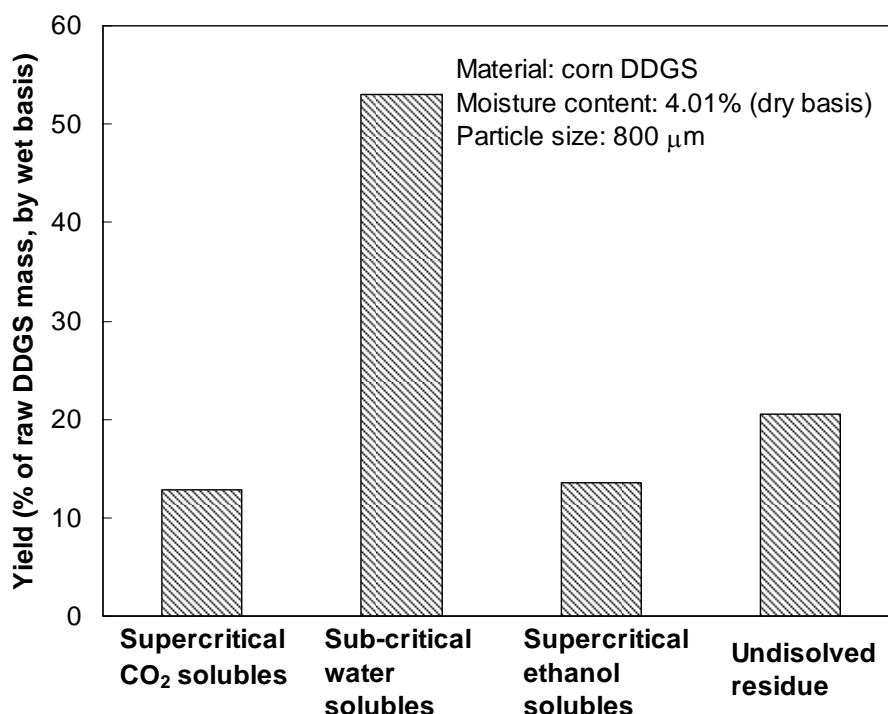


Fig. 2. Yields of supercritical CO<sub>2</sub> solubles, near- or super- critical water solubles and supercritical ethanol solubles.

The properties of solid residues after each process are given in Table 1. The average particle size of the DDGS, before and after supercritical CO<sub>2</sub> extraction, was 800 μm. There was no significant change in average particle size during supercritical CO<sub>2</sub>. However, most of the particles became powders during sub-critical water and supercritical ethanol extraction. The raw DDGS feedstock had 4.01% moisture and 7.51% ash, on a dry basis. The moisture and ash contents of the DDGS residue, after supercritical CO<sub>2</sub> extraction, were 1.62% and 5.68%, respectively, on dry bases. Parts of the water and ash were dissolved into the supercritical CO<sub>2</sub>.

The sub-critical water and supercritical ethanol further dissolved part of ash. At the end of the sub-critical water and supercritical ethanol extraction, the ash contents were 2.75% and 2.25%, on a dry basis. There were slight decreases in the bulk density of DDGS residue from 525 kg/m<sup>3</sup> to 487 kg/m<sup>3</sup> during supercritical CO<sub>2</sub> and from 173 kg/m<sup>3</sup> to 129 kg/m<sup>3</sup> during supercritical ethanol processes. However, the bulk density decreased significantly from 487 kg/m<sup>3</sup> to 173 kg/m<sup>3</sup> during sub-critical water extraction. The decreases in the bulk density were almost consistent with the weight losses of DDGS particles during extraction. This means that the release of solubles into the processing fluids did not reduce the volume of the DDGS particles and the processing fluids meanwhile might cause the swelling of the particles. The heating value of raw corn DDGS was 27.2 MJ/kg (dry basis). The heating value of DDGS residue after supercritical CO<sub>2</sub> extraction decreased to 21.8 MJ/kg because lipid components with high heating values were extracted out of the DDGS. After sub-critical water and supercritical ethanol extraction, the heating values of DDGS residue increased due to the increase of char content in the residue, which has a high heating value.

Table 1. Properties of raw DDGS and DDGS residue after supercritical fluid processing

	Raw corn DDGS	Residue after CO <sub>2</sub> extraction	Residue after CO <sub>2</sub> and H <sub>2</sub> O extraction	Residue after CO <sub>2</sub> , H <sub>2</sub> O and C <sub>2</sub> H <sub>5</sub> OH extraction
Moisture content (% , wet basis)	4.01	1.62	0	0
Particle size (μm)	800	800	-	-
Bulk density (kg/m <sup>3</sup> )	525	487	173	129
Ash content (% , dry basis)	7.51	5.68	2.75	2.25
Heating value (MJ/kg, dry basis)	27.2	21.8	28.3	31.1

### ***Thermal degradation of DDGS residue after CO<sub>2</sub> extraction in nitrogen and air***

Thermogravimetric analyses of pyrolysis of DDGS residues in nitrogen at a heating rate of 30°C/min are given Fig. 3. The pyrolysis of DDGS with 1.62% moisture (dry basis) in nitrogen occurred in the temperature range from 200°C to 650°C at the heating rate of 30°C/min as shown in Fig. 3. Before pyrolysis, drying occurred to remove the water in DDGS. The maximum pyrolysis rate of DDGS with 1.62% moisture in nitrogen at the heating rate of 30°C/min was 13%/min (wet basis), which was achieved at the temperature of 375°C. The residual weights of DDGS in nitrogen at 650°C almost became constant at 27% of the original dry mass of DDGS with 1.62% moisture as shown in Fig. 3.

Thermogravimetric analyses of oxidation of DDGS residue with 1.62% moisture in air at a heating rate of 30°C/min are shown in Fig. 4. There were two obvious oxidation zones as shown in Fig. 4. The starting temperatures of the first and second oxidation zones were 200°C and 470°C, respectively. As shown in Fig. 4, the maximum oxidation rate in the first zone was much higher than that of the second zone. In the first zone, some volatiles in DDGS were released and oxidized at a low temperature and high rate. In the second zone, the char and more thermally stable components, such as lignin, continued to be oxidized at higher temperatures and lower rates. For the DDGS with 1.62% moisture, the maximum oxidation rates of the first and second zones at the heating rate of 30°C/min were 22.5 and 4.6 %/min (wet basis), respectively, as shown in Fig. 4. The temperatures for the maximum oxidation rates of the first and second zones were 405°C and 720°C, respectively. As shown in Fig. 4, the residual weight of DDGS in air at the end of the first oxidation zone was about 43% of the original dry mass of DDGS with 1.62% moisture. The remaining solid residue at the end of the first oxidation zone may have been char and more thermally stable components such as lignin in the DDGS. With a further increase in temperature to 850°C, the residual weight became almost constant at 5.5%

of the original dry mass of DDGS. The remaining solid residue at the end of the second oxidation zone was ash. The ash content of the DDGS sample, after extraction of their lipids, was 5.68% on a dry basis as given in Table 1.

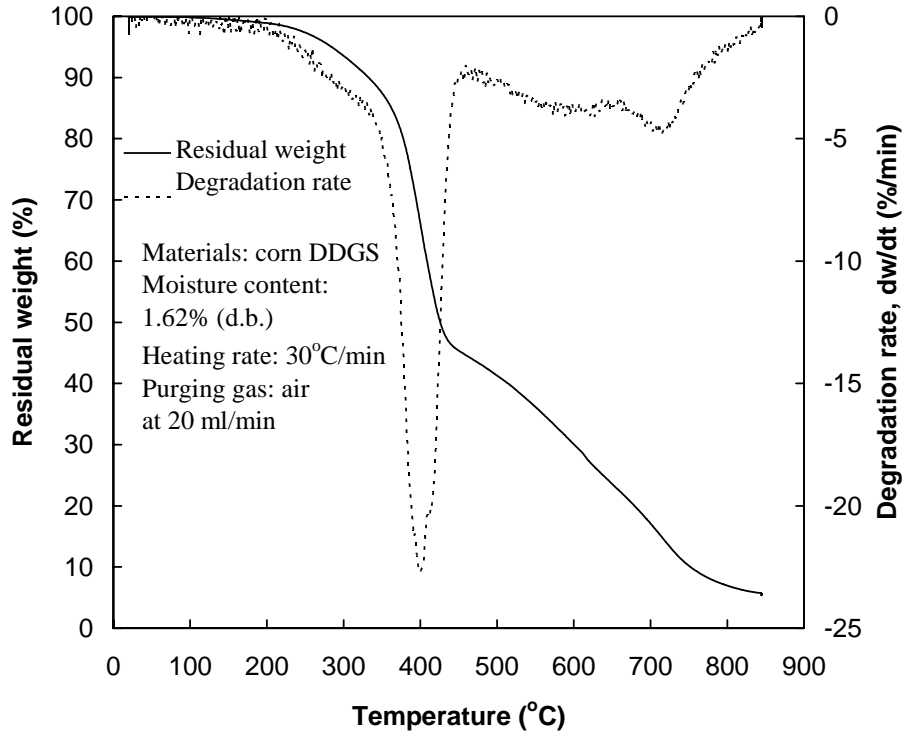


Figure 3. Thermal degradation of corn DDGS residue in nitrogen.

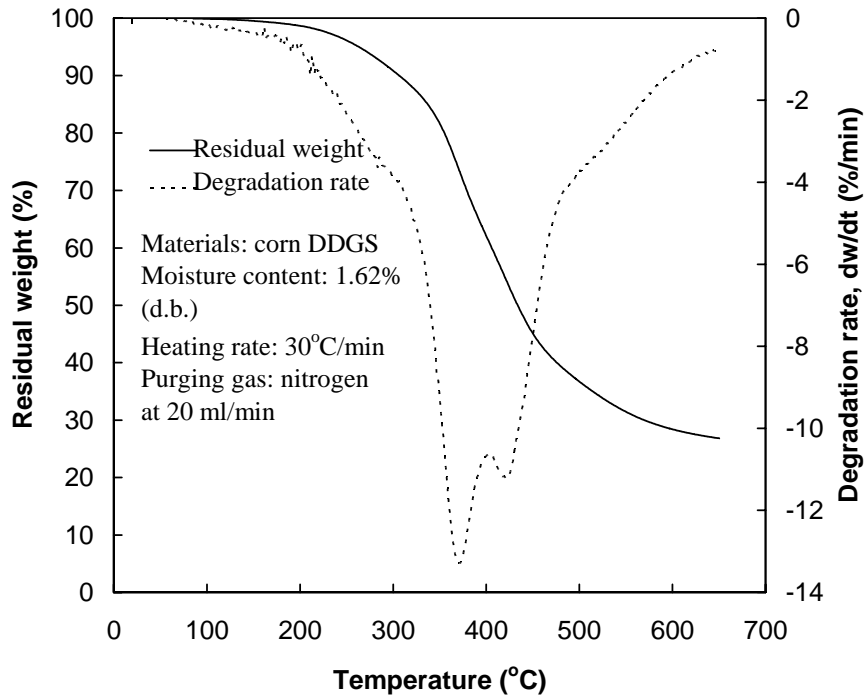


Figure 4. Thermal degradation of corn DDGS residues in air.



## Conclusions

Supercritical fluid processing and thermochemical conversion technologies have been used to recover high-value chemicals and energy products from DDGS. During a sequential supercritical fluid process, 12.8%, 53.1% and 13.6% of the raw DDGS with 4.01% moisture and 7.51% ash on wet basis were dissolved in supercritical CO<sub>2</sub> at 70°C and 27.5 MPa, sub-critical water at 225°C, and 24 MPa and supercritical ethanol at 250°C and 10 MPa, respectively. Only about 20.5% of raw DDGS mass was undissolved by the three solvents under the given operating conditions. Parts of the water and ash were dissolved into the supercritical CO<sub>2</sub>. The sub-critical water and supercritical ethanol further dissolved part of ash. There were slight decreases in the bulk density of DDGS residue during supercritical CO<sub>2</sub> and supercritical ethanol processes. However, the bulk density decreased significantly during sub-critical water extraction. The heating value of raw corn DDGS was 27.2 MJ/kg (dry basis). The heating value of DDGS residue after supercritical CO<sub>2</sub> extraction decreased to 21.8 MJ/kg. However, the heating values of DDGS residue increased to 31.1 MJ/kg after sub-critical water and supercritical ethanol extraction.

The pyrolysis of DDGS with 1.62% of moisture (dry basis) in nitrogen occurred in the temperature range from 200°C to 650°C at the heating rate of 30°C/min. The maximum pyrolysis rate of DDGS with 1.62% moisture in nitrogen at the heating rate of 30°C/min was 13%/min (wet basis), which was achieved at the temperature of 375°C. The residual weights of DDGS in nitrogen at 650°C almost became constant at 27% of the original dry mass of DDGS with 1.62% moisture. There were two obvious oxidation zones during thermal degradation of DDGS residue in air. The starting temperatures of the first and second oxidation zones were 200°C and 470°C, respectively. The maximum oxidation rates of the first and second zones at the heating rate of 30°C/min were 22.5 %/min (wet basis) at 405°C and 4.6 %/min (wet basis) 720°C, respectively. The residual weight of DDGS in air at the end of the first and second oxidation zones were about 43% and 5.5% of the original dry mass of DDGS, respectively.

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