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Investigating the insecticidal activity of lignin, cellulose and hemicellulose bio-oil

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Introduction

- Agricultural and forestry residues are primarily composed of:
 - lignin (L)
 - cellulose (C)
 - hemicellulose (H)
- C and H have industrial use (e.g., in paper production)
- 40-50 million tons of L per annum produced worldwide, currently a waste product
- Biomass conversion to produce high value pesticides



Introduction

Biomass	L	C	H	Other
Eucalyptus	29	48	14	9
Sugarcane	11	22	15	52
Corn stover	17	36	23	24

- Biomass contains varying proportions of lignin, cellulose and hemicellulose
- Bio-oils from a range of biomass have varying insecticidal activity

Objectives

- Compare the insecticidal activity of bio-oils produced from L, C and H biomass components
- Compare the insecticidal activity of the *mixture of bio-oils* ($L_{oil}+C_{oil}+H_{oil}$) and *mixture of biomass* (L+C+H)
- Synergy?
 - Greater than additive effects
 - Lower concentrations can be used:
 - Smaller environmental impact
 - Cheaper

Definitions:

Mixture of Bio-oils = bio-oils produced from individual biomass components were combined on the basis of their yield

Mixture of Biomass = bio-oil produced from combination of biomass components in equal parts

Experimental Biomass

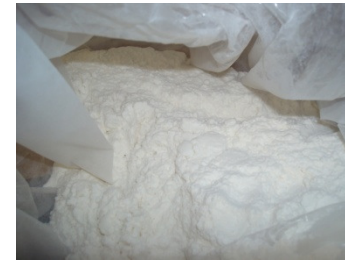
Lignin

- particle size < 200 μm
- derived from wood
- Organosolv lignin



Cellulose

- particle size < 500 μm
- derived from plant source

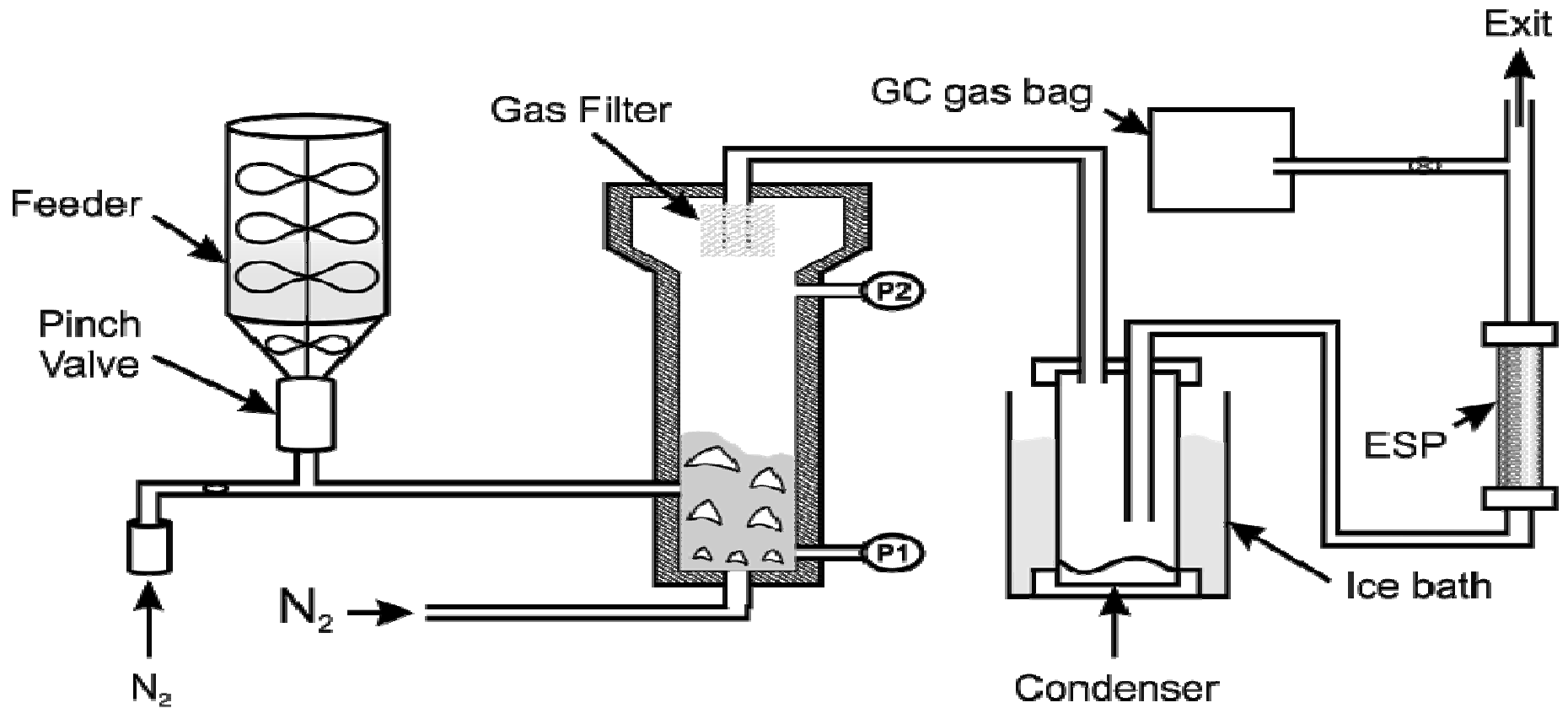


Hemicellulose

- particle size < 800 μm
- obtained from birch wood



Experimental

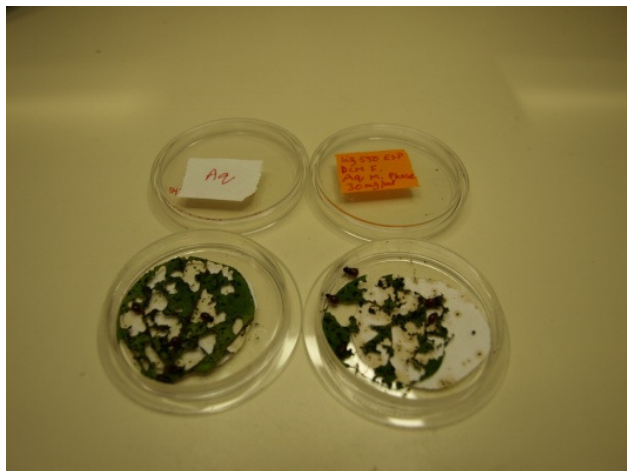


- Fluidized bubbling bed of sand
- Pyrolysis at 550°C
- Vapor Residence Time: 2.3 s

Experimental

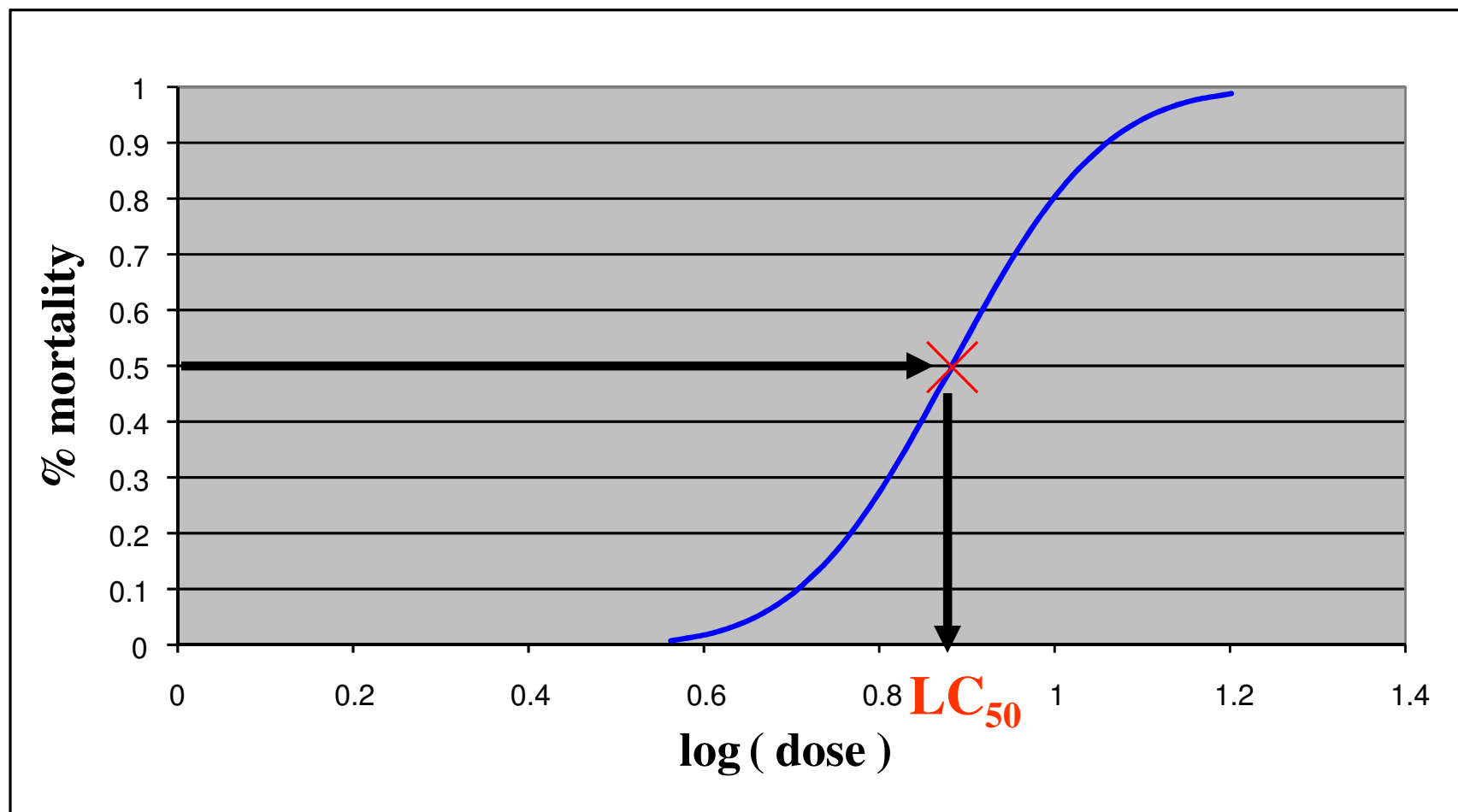
CPB 2nd instar larvae bioassay

- Potato leaf (*Solanum tuberosum* var. Kennebec) discs were treated with control or bio-oil (150 μ l)
- Five Colorado potato beetle 2nd instar larvae (*Leptinotarsa decemlineata* (Say)) were placed on each treated disc
- Mortality of larvae was recorded after 48 h
- All insect bioassays were held in an environmental chamber at 25° C, 50% RH



Experimental Determination of LC_{50}

Example: LC_{50} (mg/ml) of the lignin bio-oil



Experimental Synergism Determination

$$S = M [X_L / L + X_C / C + X_H / H]$$

M, L, C and H : LC₅₀s of the *mixture of bio-oils*, and L, C, and H oils

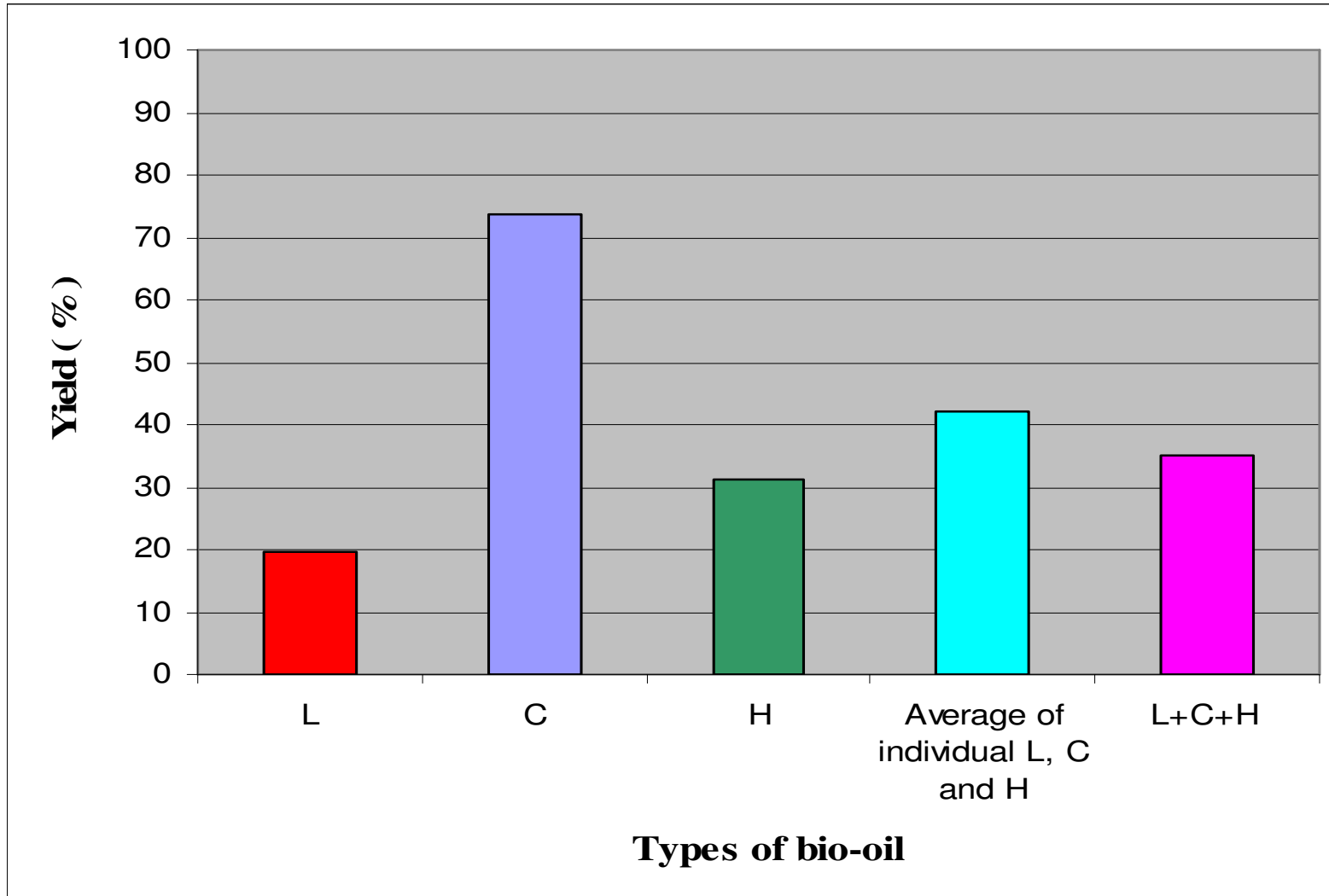
X_L, X_C, X_H : weight fractions of L, C, and H oils in the *mixture of bio-oils*

- S > 1 (Antagonistic toxicity)
- S = 1 (Additive toxicity)
- S < 1 (Synergistic toxicity)

Marking, L.L., Method for assessing additive toxicity of chemical mixtures. 1977, 99–108.

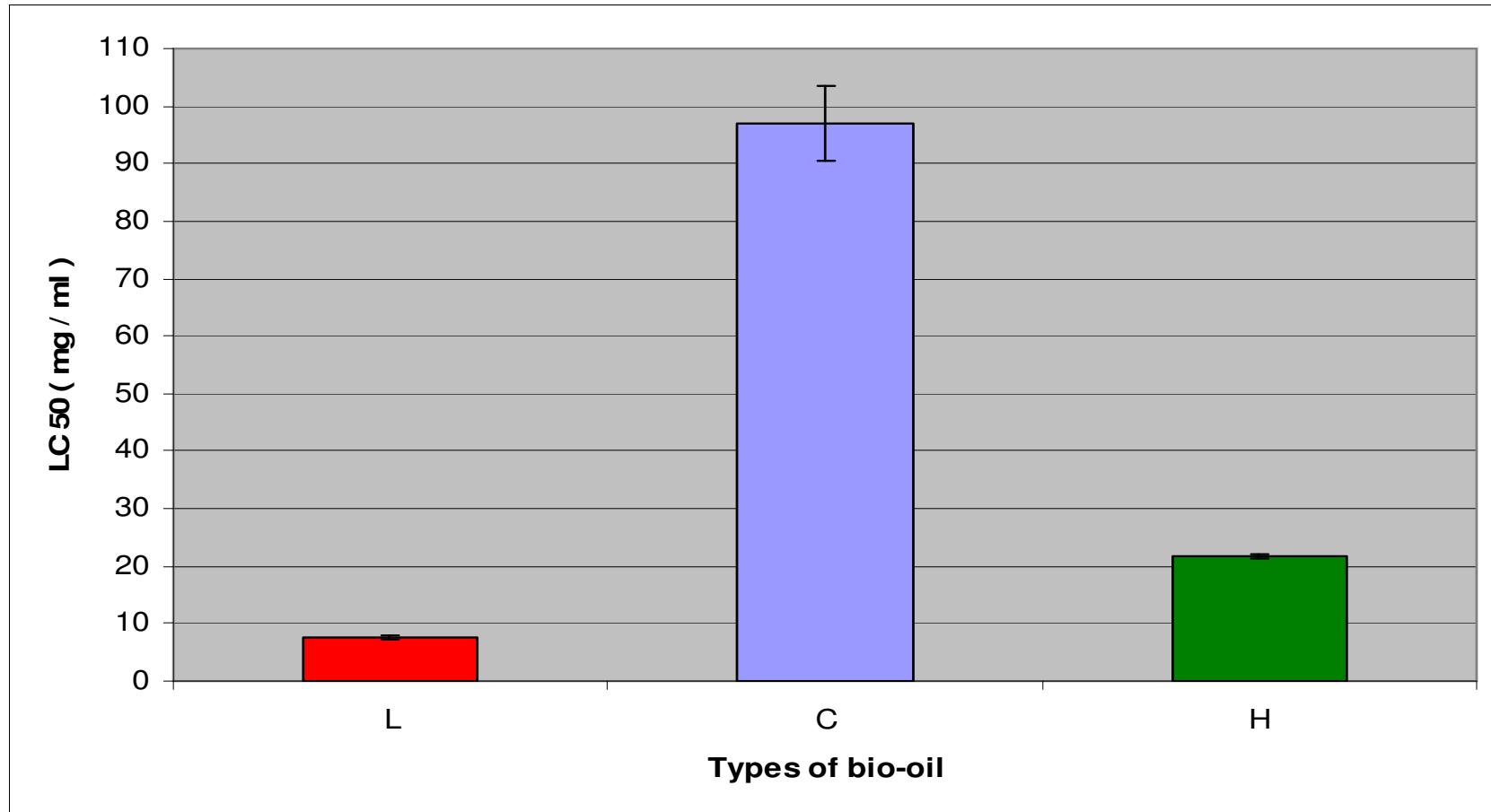
Results

Bio-oil yield (%) from L, C and H and *mixture of biomass*



Results

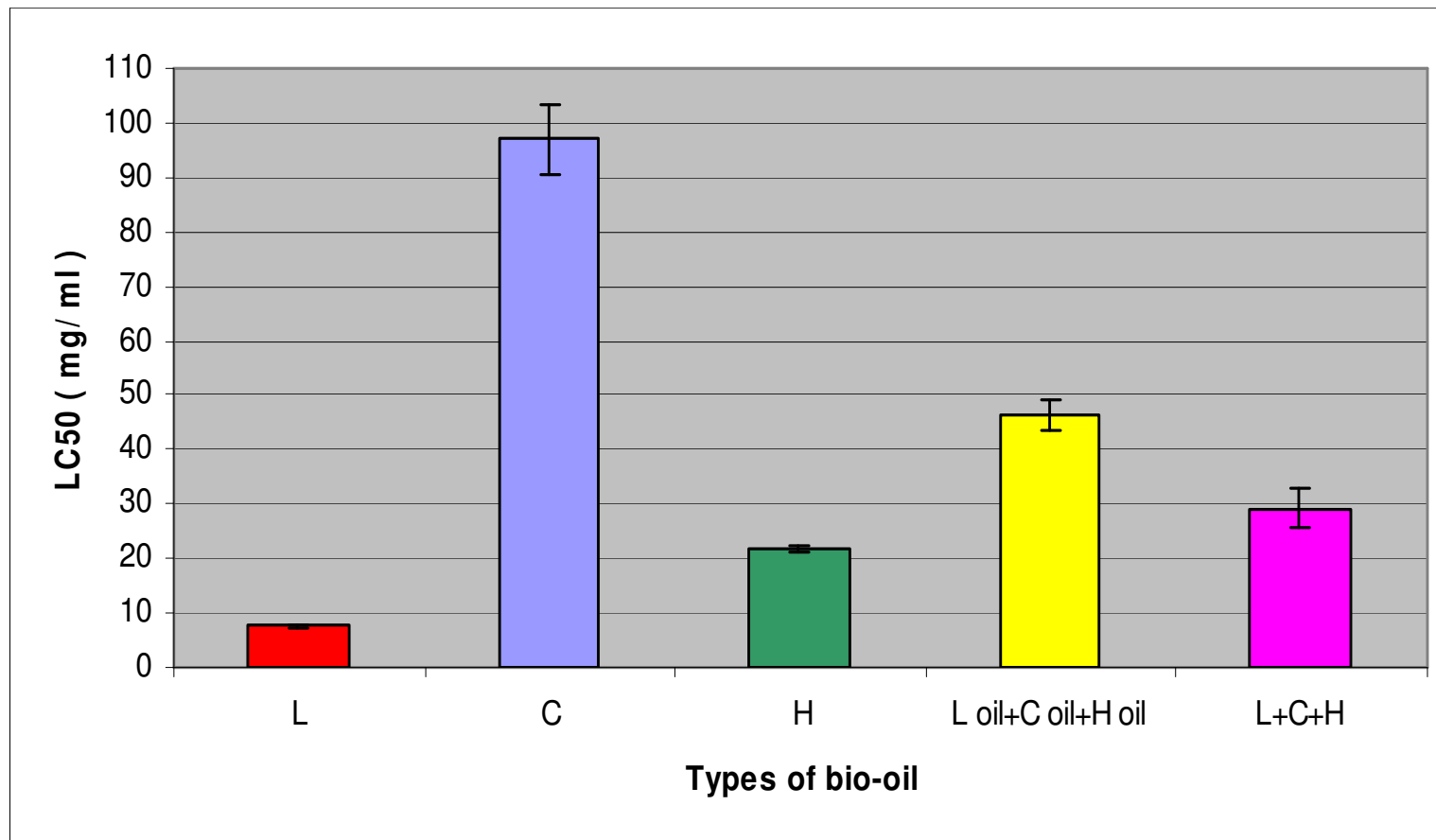
L more effective insecticide than C and H bio-oil



48 h LC₅₀ (95% C.I.) values for L, C and H bio-oil with 2nd instar Colorado potato beetle

Results

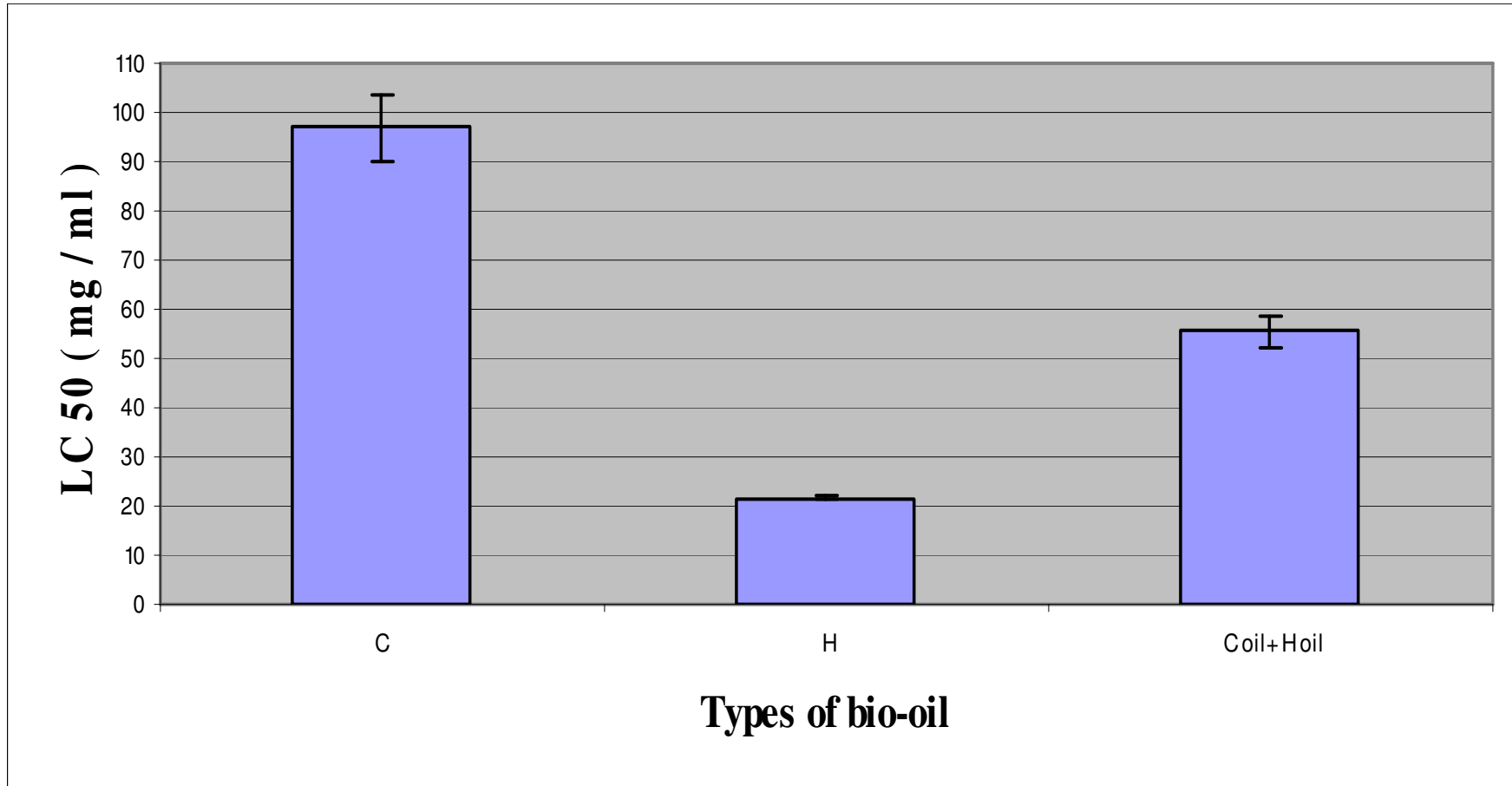
L, C and H bio-oil combination produced antagonistic effect ($S= 1.36$)



48 h LC₅₀ (95% C.I.) values for L, C, H, *mixture of bio-oil* and *mixture of biomass* with 2nd instar Colorado potato beetle

Results

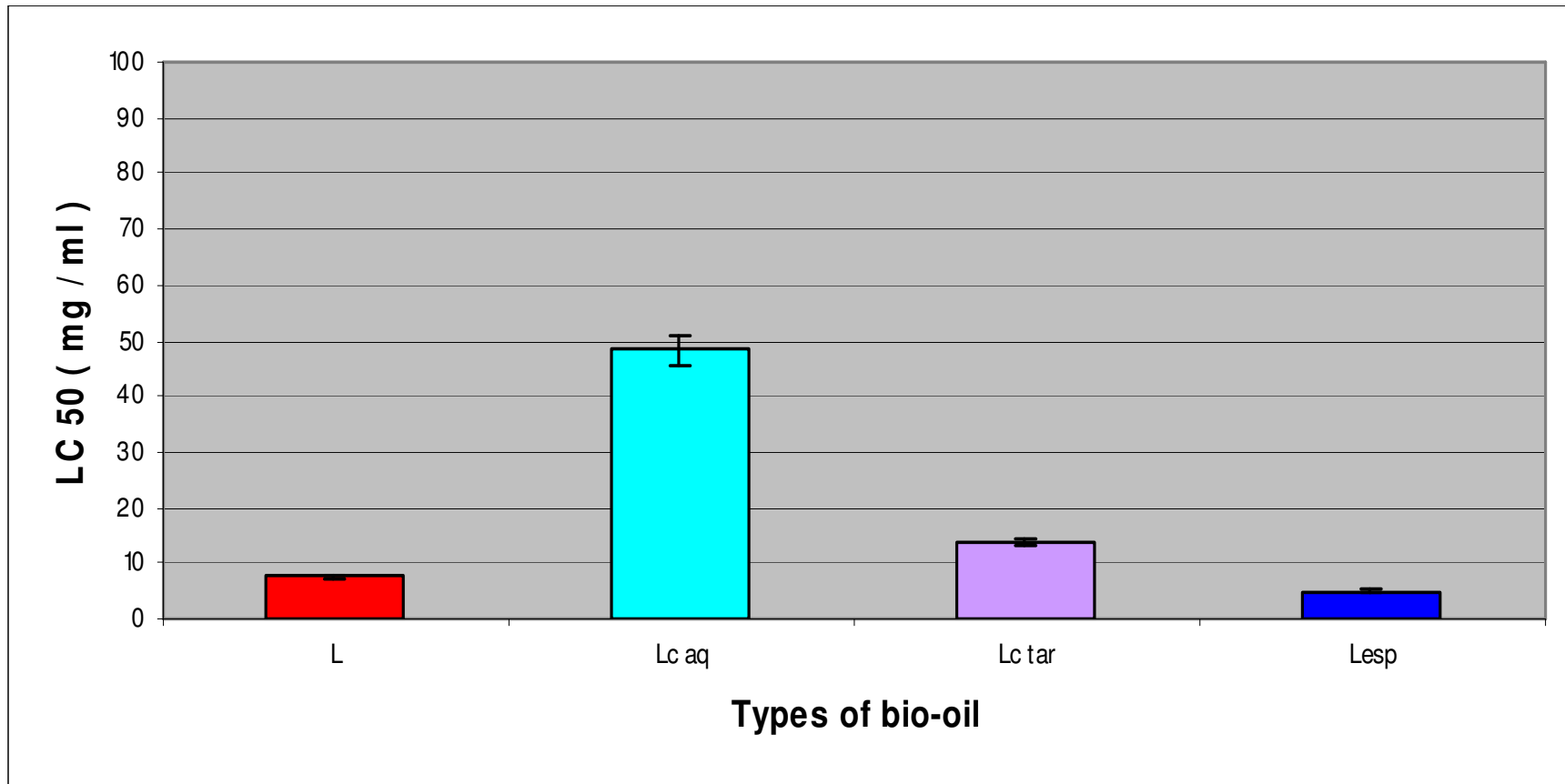
Combination of C and H bio-oil produced synergistic effect ($S = 0.82$)



48 h LC₅₀ (95% C.I.) values for C, H and Coil + Hoil with 2nd instar Colorado potato beetle

Results

No interaction between L bio-oil fractions (additive toxicity , $S = 0.98 \approx 1$)



48 h LC₅₀ (95% C.I.) values for L, Lc-aq, Lc-tar, and Lesp with 2nd instar Colorado potato beetle

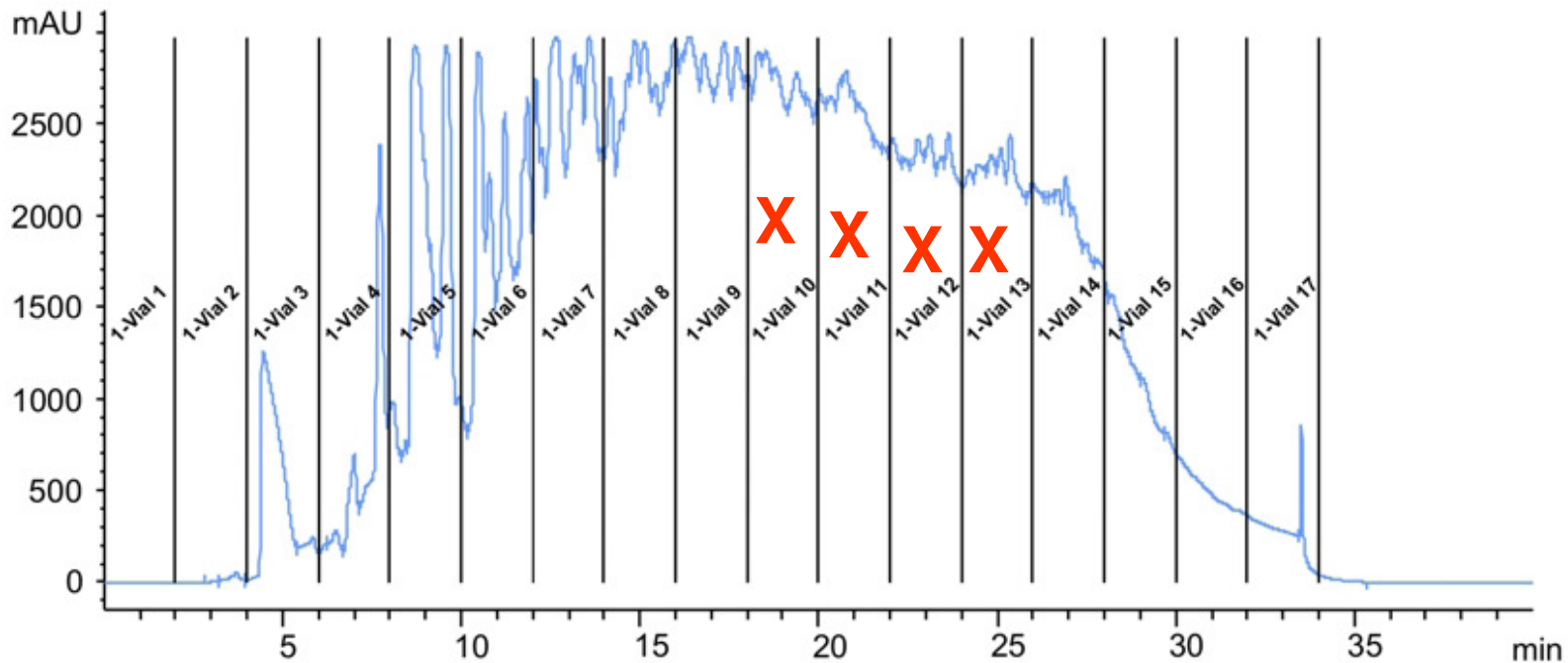
Conclusion

- To maximize the insecticidal activity:
 - (1) Separate lignin fraction and pyrolyze it
 - (2) Use only the lignin ESP bio-oil fraction
- Further research is recommended to investigate the toxicity of the *mixture of bio-oils* in which the L content is higher than the other two principal components

Future Projects

Separation and identification of active lignin ESP bio-oil components

HPLC chromatograph for lignin bio-oil sample



Time (m)	0	2	20	25	30	31	40
Water	90	75	25	0	0	90	90
Acetonitrile	10	25	75	100	100	10	10

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